BOD

COD

BTX

TOC

DOC

UV254

NO3

NO2

NH4

K+

Free Chlorine

F-

TSS

Turbidity

Color

pH

ORP

EC

Temperature

O2

O3

H2S

AOC

Fingerprints

Alarm

s::can
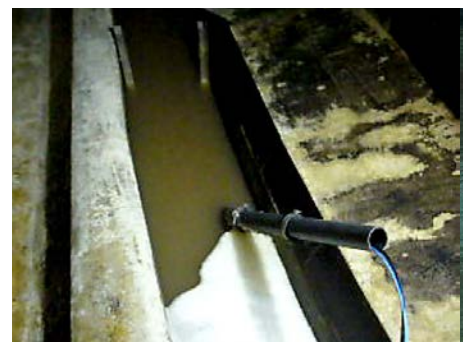Intelligent. Optical. Online.

Industrial applications & Hydrocarbons/Oil-in-Water

www.s-can.at

1 Monitoring and Control of a Paper Mill WWTP

:: Figure 1 below depicts typical and reproducible spectra at various process measuring points of a paper mill WWTP.

:: The spectra increase steadily with decreasing wavelength, which is characteristic of the influence of undissolved particles (f " = 0). Only the relative maximum at 280 mm is distinct from the influence of the turbid substances, due to the absorbance by dissolved organic substances, mainly ligninic acids. This shoulder is caused by carbon compounds which, from the biological point of view, can be accessed relatively easily. Comparison of absorbance spectra of inflow, pretreatment and outflow distinctly shows the decrease of this peak, indicating the biological degradation of the organic substances in the course of the treatment and, following local calibration, allowing clear differentiation between COD and BSB5.

:: In general, however, the plant can best be controlled without calibration to conventional parameters, merely on the basis of overall spectral information. Conventional calibrations are now merely carried out for purposes of reference checking the instrument.

:: Experience has shown that a parameter describing the dissolved organic substances is particularly suitable for operation and/or control of the treatment performance of a plant.

:: This important information can only be gained from spectral measurements. This waste water cannot be well monitored by a simple UV probe, since the SAC254 does not strongly correlate with the degradable carbon.

Additional literature: F.M. Muzio et al.: "BOD5 Estimation for Pulp and Paper Mill Effluent Using UV Absorbance" Water Research Vol. 35, No.7, pp.1842-1850, 2001
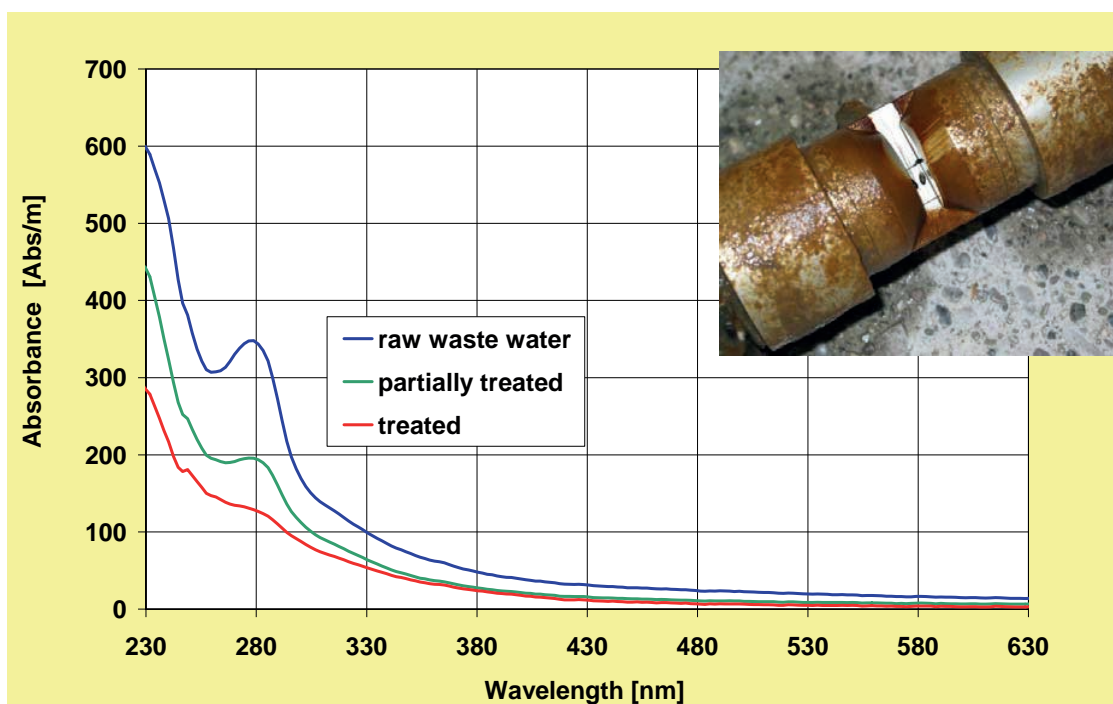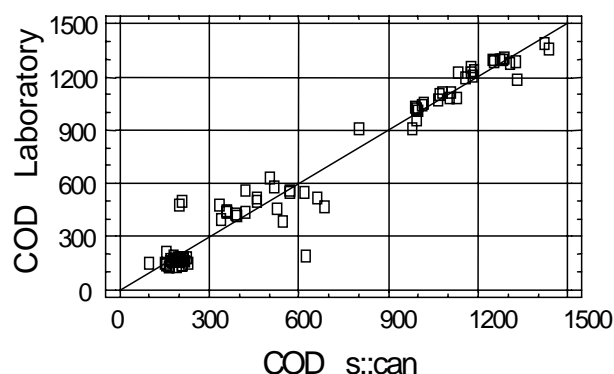
Figure 1: Absorbance spectra of waste-water samples at various measurement points

2 Electroplating industries: Monitoring the Effluent of an Industrial Factory with Varying Process Agents

:: The following figures illustrate the daily contours of the UV/VIS spectra in the runoff of an industrial WWTP. There is a one-hour interval between spectra. A pronounced time-dynamic behavior can be seen and individual substance groups can be clearly distinguished:

:: They are comprised of organic carbons of the Group A (250 – 290 nm: low molecular compounds, aromatics, proteins, short-chain aliphatics, organic solvents, etc.), Group B (290 – 350 nm: organic and humic acids, products of biological degradation, etc.), and Group C (350 – 380 nm: no allocations to date – in any case, no simple colorants as yet).
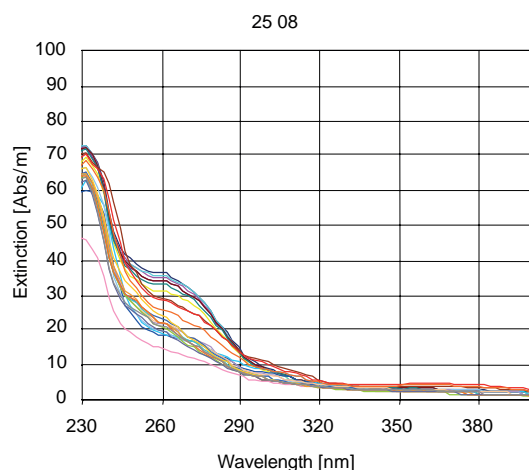

Figure 2: Relatively calm behavior; movement perceptible only in the organic-carbon Area A (250-290 nm); turbidity relatively constant
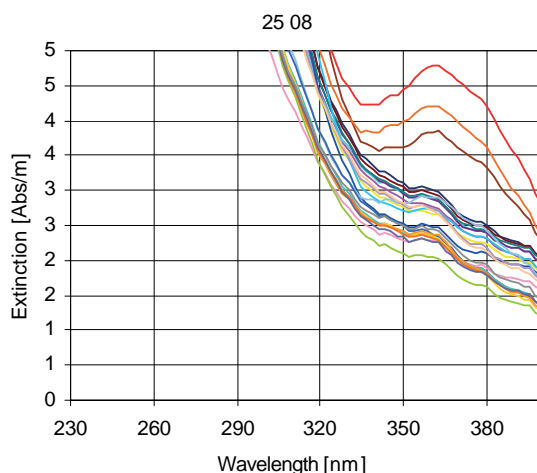

Figure 3: Same day, different scale: now a peak in the carbon Area B (350-380 nm) is also perceptible.
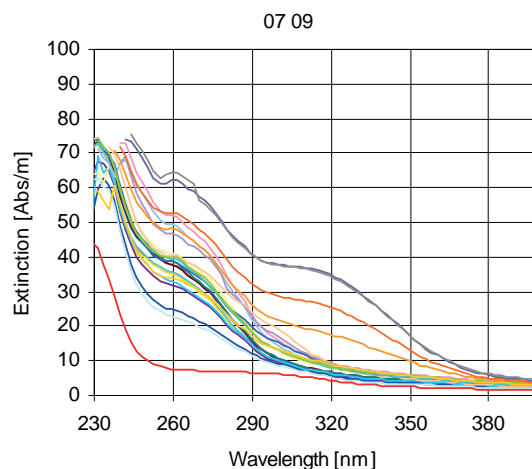

Figure 4: Extremely high degrees of turbidity; high values also in carbon Area A over a short time; short peak in Area C: very pure water for a short time (rinsing water?)
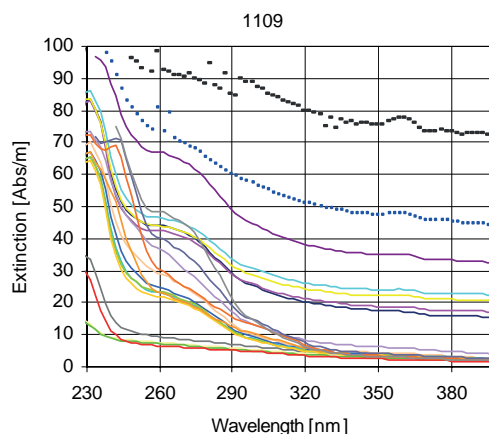

Figure 5: Significant difference between carbon Areas A and B; extreme peak of B on Sept. 7 at midnight. 1 very pure spectrum (rinsing water?)

:: Allocation and calibration to processes and process-related chemicals would enable the assessment of substance groups and the establishment of internal alarm parameters (in the sense of retention of toxic substances). The COD itself has only very restricted indicative potential as a sum-parameter for such an operation.

3 Monitoring of Cooling Liquids / Oils

:: The fresh coolant is set as a reference spectrum = 0; changes become spectrally visible through water diffusion / de-emulsification / as well as combustion products / color

:: Measurement has a true resolution of > 1:100; thus, the degree of change can be given with sufficient precision (accuracy) in %.

:: No substance concentrations are calibrated, since classic parameters cannot describe the processes involved with the same sensitivity and selectivity.

:: Sudden deviations from the reference spectrum can be applied as a very sensitive, broadband alarm parameter.

:: Application was successfully tested for:
- transformer oil and for an automobile factory.

monitoring of cooling liquids

Color from burt components

Water in oil

Used cooling liquid

New cooling liquid = reference = 0

Extinction [Abs/m] vs Wavelength[nm]
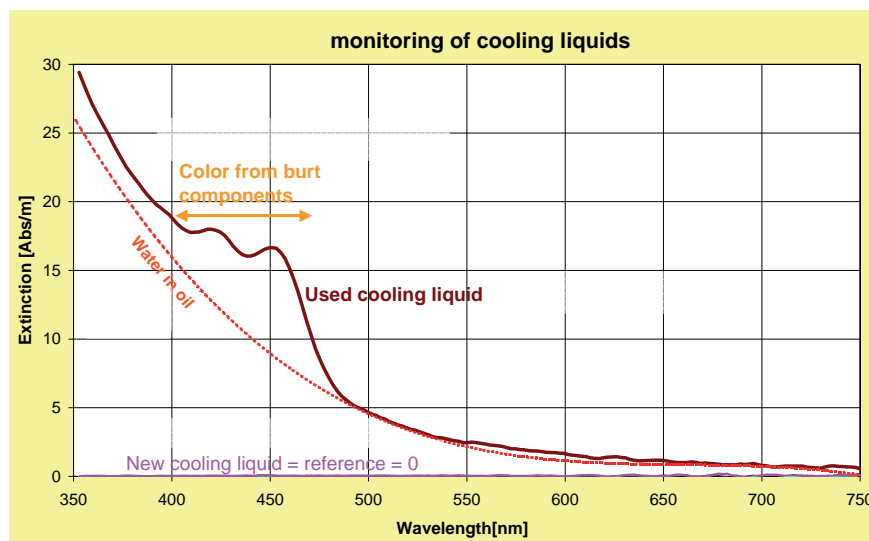
4 Beverage Industries

4.1 Comparison of Two Types of Red Wine

In Figure 6, the individual substance groups which characterise two types of red wine from the same Italian area can be distinguished in the spectrum or delta spectrum, respectively:

1) Coloration in the visible range: red coloration (shoulder at 620 nm), as well as the yellow/brown coloration (broad shoulder or valley at ca. 500 nm) can be recognized, which can already exceed visual checking at this stage.

2) Organic acids, tannins, etc. between 280 and 350 nm . . . the substance groups which are said to be primarily responsible for the taste.

3) Alcohols, other fermentation products, aromates, between 230 and 280 nm.
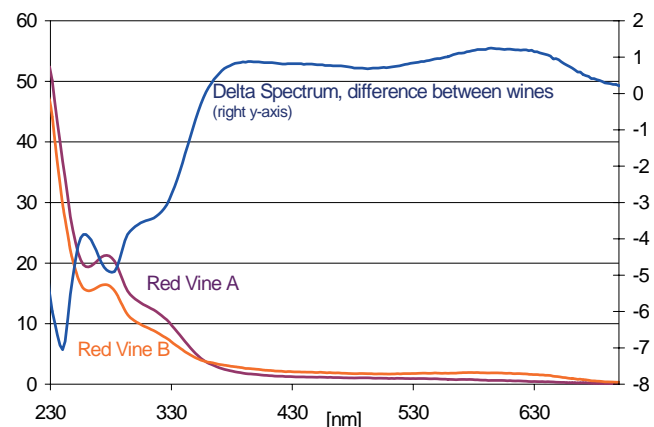
Delta Spectrum, difference between wines (right y-axis)

Red Vine A

Red Vine B

Figure 6: The absorption spectra of two different red wines and the Delta-Spectrum showing the difference between the wines

4

:: It can be anticipated from the results that, with the help of this method, the quality of wines - and as well other alcoholic or non-alcoholic beverages - can be checked and distinguished in process.

:: Deviations from a target status can be detected and used i.e. for product quality surveillance or for blending.

4.2 Comparison of Three Types of Beer

The spectral comparison of different types of beer of one brand show distinctive differences. This kind of "finger-print" information alone opens a wide horizon of possibilities for the beverage industry, from product composition, component control up to product quality end control.
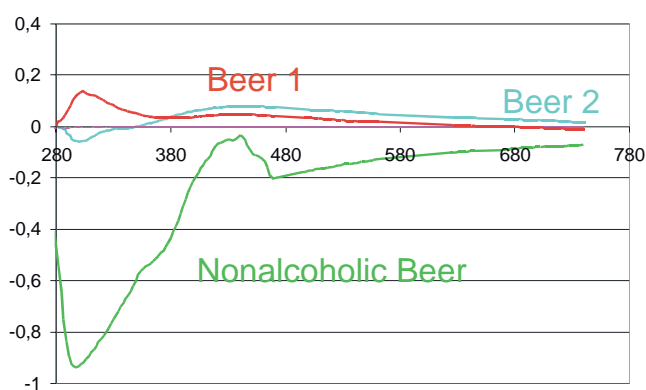

Figure 7: Absorption spectra of three types of beer

Also for non alcoholic beverages, a broad range of applications can be developed based on process UV spectrometry, like distinguishing between fruit sirups, mixing and diluting of sirups, alarm in case of quality problems with basis components, etc.

5 Monitoring the Effluent of a Dairy

:: In a dairy's effluent, online spectra are measured by a spectro::lyser™ in order to identify peaks at an early stage and to keep them away from the municipal WWTP.

:: No drift whatsoever could be identified, even at high fat concentrations. The automatic pressure air cleaning keeps the windows 100 % free of deposits. Maintenance is almost zero.

:: Spectral features allowed the very clear identification and stable calibration of COD and BOD in the whole range up to 20 g/l COD by automated chemometric methods (see Figure 8).
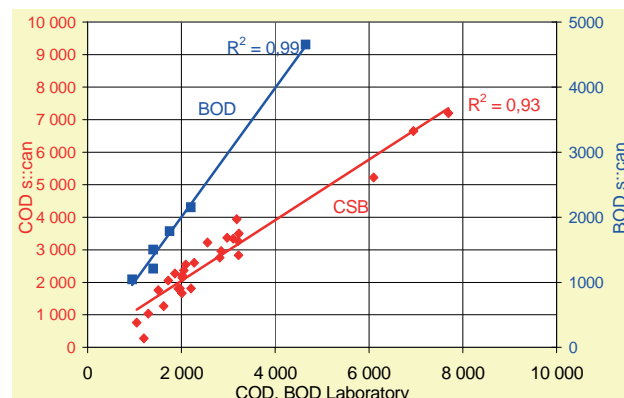

Figure 8: Correlation between laboratory results and the results measured with the s::can probe
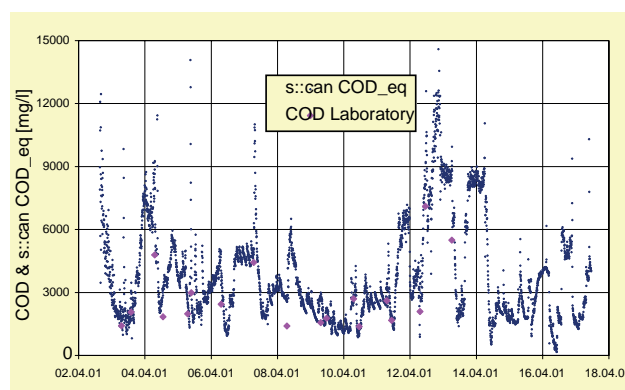

Figure 9: s::can and laboratory COD measurements

:: The observed strongly dynamic behavior, represented in above figure, allows the identification of different diary processes (mainly washing/flushing processes) and clearly detects irregular charges.

:: With the help of this information, the diary has now a means to optimize the charge distribution.

:: The WWTP manager can monitor charges and peaks and receives alarms without delay so he can react immediately if necessary.

5

6 Hydrocarbons / Oil

6.1 Detection with UV/Vis Spectrometry

Detection of the presence of hydrocarbons and oils in water is an important application in some industrial waste waters (petrochemical applications, but also food industry, e.g. in edible oil production) as well as in environmental monitoring (river, lake, seawater). Hydrocarbons and oil are groups of substances and should thus be considered sum parameters. However, unlike COD or TOC, they are not intended to represent the total amount of organic materials present in the water, but a more specific fraction.

Hydrocarbons

Hydrocarbons, as defined in water quality monitoring, are substances originating from or produced out of crude oil and natural gas.

This group comprises a huge amount of different molecules, ranging from aromatic substances (e.g. benzene) to linear alkanes (e.g. hexane). The signal in the UV-absorption spectrum for these substances varies with their

> **The signal in the UV-absorption spectrum for hydrocarbons varies with their chemical structure.**
> **Depending on the application about 30 - 80 % of the substances produce a useful optical signal.**

chemical structure, but it is known that depending on the application about 30 - 80 percent of the substances that contribute to the parameter Total Hydrocarbons produce a useful optical signal, either by conjugated double-bounds, or by chromophore functional groups.
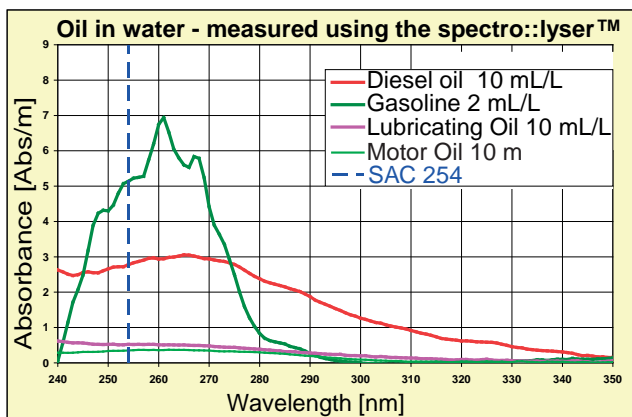

Figure 10: Spectra of different hydrocarbons in water.

Concerning hydrocarbon concentration estimation, the direct spectrometric method is applicable only to those oil-in-water samples in which the emulsified oil contains aromatic fractions or functional groups which absorb in the UV region. Most crude and petroleum oils contain a significant proportion of aromatic compounds, typically representing 20 - 60 % of the total hydrocarbons.

Aromatic compounds

Common aromatic compounds present in crude oils include benzene / BTX, alkylbenzenes, alkylnaphthalenes, biphenyl, alkylbiphenyls, phenanthrene, alkylphenanthrenes, and aromatic steranes, all of them well detectable in the low ppb range in practical applications except highly turbid or strongly colored waters. The EPA-PAH are the 16 most important polycyclic aromatic hydrocarbons, which are rated high priority pollutants because of their toxicity and their ubiquity.
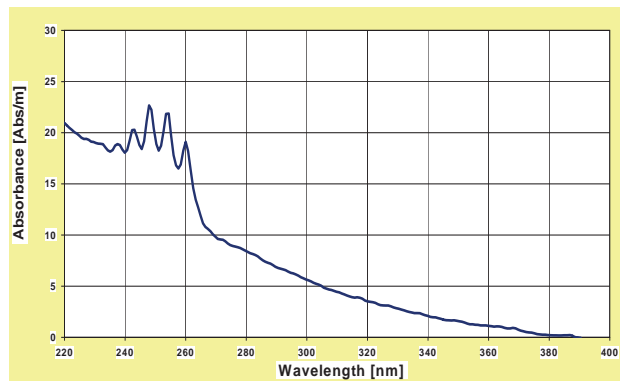

Figure 11: Spectrum of Benzene in ground water

Refined oils

The lighter, refined oils, such as diesel oil and gasoline, contain a higher fraction of short linear alkanes and lower percentages of unsaturated and aromatic substances. This reduces their absorption signal in the UV-spectrum. On the other hand, the smaller molecules in these products mean their solubility in water becomes higher. This is a useful feature because naturally oil and hydrocarbons mix poorly with water.

This means the oil will either float on the surface of the water or is emulsified, meaning it is present as small droplets of oil floating in the water. This non-mixing behaviour makes any kind of online detection difficult as the optimal place for sampling is not always the same; for one product it could be the surface, for the other sub-surface. As the spectro::lyser™ needs to be submerged to operate properly, only emulsified and dissolved parts of oils will be detected.

Therefore, the possibility of measurement of hydrocarbons / oil in water using UV/Vis spectrometry strongly depends on the composition of the oil, and more specifically on the following points:

:: **aromatic content ->** responsible for the main absorption signal

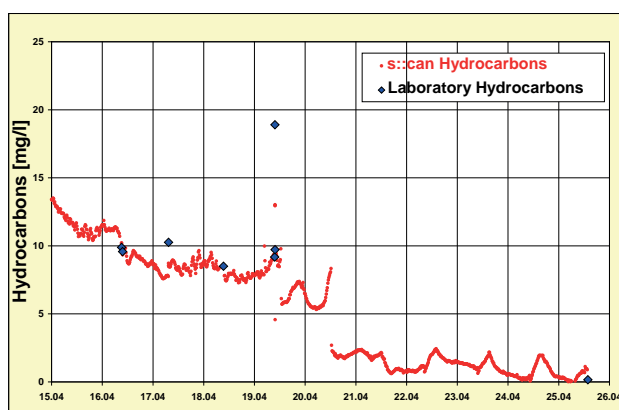:: **size of the molecules ->** determines miscibility

Figure 12: Results of online hydrocarbon measurements using a spectro::lyser™ compared with laboratory results.

6.2 Possible applications

In general, it can be stated that online UV-spectrometry can be used to monitor total hydrocarbons in applications such as primary oil production effluents and discharges, monitoring of cooling water in petrochemical plant for product ingress and the detection of accidental spills into surface waters. The method is generally not applicable for the measurement of alkane-based oils and greases or for vegetable oils and fats (due to their low content of aromatics).

Regarding hydrocarbon detection limits, s::can has practical experience with:

:: Benzene, and other aromatics in clear water: down to 0.05 ppm, changes of 0.01 ppm (with 100 mm path length)

:: Gasoline oil, light crude oils etc. in river water: down to 1 ppm depending on aromatics content, selectivity depends on matrix

:: Related application examples are in Slovnaft Bratislava and MOL Szazhalombatta oil refineries to control discharge input and output of water treatment plants, circulation waters and process waters, and more applications in the oil industry world wide. Alarming limit is typically 1 ppm of Oil in most applications, on trade waste water background.

A big advantage is the **maintenance-free operation of spectro::lysers** even in highly concentrated waters, even with quickly attaching charged solids, because of the very effective automatic pressure air cleaning.

It has to be stressed that growth of biological matter on windows is no practical issue since the UV Xenon lamp is a disinfectant that does not allow bacteria to populate the windows.

If the sensitivity of the direct method should not be sufficient, or the solubility should not be constant, a multi-purpose by-pass fitting allows the automatic addition of a harmless solvent like isopropanol in order to improve the solubility and thus the signal.

> **If the sensitivity of the direct method is not sufficient a multi-purpose by-pass fitting allows the addition of a solvent to improve the solubility and thus the signal.**

In addition, it is possible to estimate non-dissolved oils / emulsions / oil droplets / by their scattering properties.

Detection of oil or hydrocarbons, however, always remains a function of the precise product to be measured and the application. It is possible that the signal is too weak for detection in a specific application, especially when alcohol, greases, vegetable oils and fats, or i.e. linear hydrocarbons are the predominant fraction. Therefore, for hydrocarbon and oil applications, it is strongly recommended to always perform a short feasibility together with

s::can to evaluate whether your application is possible.

Suggested Experiments:

In order to predict exact detection limits, two types of lab experiments should be conducted:

1) Use a co-solvent and investigate the spectral signal of the real crude oil of interest in solution. By this, it can be exactly indicated at which concentration level will be the detection limits *IF* the oil dissolved.

2) Simulate the given environmental conditions, related to water type, temperature, pressure, contact time, agitation of the water and see much of the oil will actually dissolve at varying conditions.

In addition, s::can uses specific spectral alarm software based on derivative spectrometry that can learn the typical optical pattern of a water, with all its normal fluctuation, and will alarm on any pattern deviation that is larger than normal fluctuation. As sea water is typically low organic, low NO3, and rather stable, the often used "hydrocarbon alarm" can be set very sensitive.
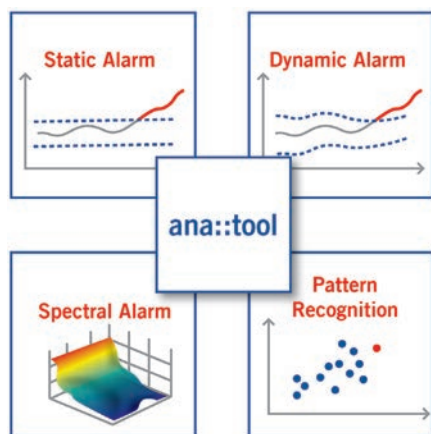

Figure 13: The s::can software module ana::tool combines Static Alarms, Dynamic Alarms, Pattern Recognition and Spectral Alarms to detect any deviation from normality.

6.3 UV/Vis Spectrometry compared to alternatives

The online measurement of oil in water remains troublesome for any technique offered for this purpose. The poor mixing behaviour is the main cause for this. The classical oil monitor measures the index of refraction of the water surface. Using this value it is possible to estimate the presence of oil floating on the surface. This provides, however, no information on the nature of the oil nor on the amount of oil present. The other established alternative is the measurement of fluorescence. Some constituents of the oil, especially aromatics, will produce a fluorescent signal when illuminated by a powerful light source.

Measuring the fluorescent signal will provide information on the substances present in the water. As with UV/Vis spectrometry, only a part of all substances is visible using this technique. Furthermore, the same issue with mixing of oil and water makes the measurements complicated. Also, when used to monitor natural waters or cooling water that is obtained from natural waters, a rather strong background signal is present. This is caused by the many organic species naturally present, such as humic acids and algae that produce a strong fluorescent signal.

Finally, full spectrum UV/Vis spectrometry is superior to SAC254 for oil measurement as many oils produce a maximum signal at other wavelengths than 254 nm (see Figure 10). As a result, the spectro::lyser™ has higher sensitivity because it can use the point in the spectrum where the signal is the strongest. Furthermore, the multiple wavelengths allow an indication of the nature of a contaminant due to shape analysis, something which the totally non-specific SAC254 parameter does not allow.

6.4 Single Organic Substances

The detection and even identification of single substances is possible using UV/Vis spectrometry. For detection, a substance needs to have an absorption signal that can be picked out from the background absorption signal. For true identification, a characteristic spectral shape is required in addition to sufficient absorption.

In case of detection of single components, s::can uses advanced chemometric methods to analyze spectral information and establish the combinations of wavelengths to use for measuring the species of interest. In this type of application, it is recommended to use the UV version of the spectro::lyser™ because its higher resolution provides

8

better possibilities in shape recognition, which is crucial for substance identification.

Some **examples of single substances** that can be detected and identified based on spectral shape are:

:: Benzene

:: Toluene

:: Xylene

:: Phenol

:: Chlorophyll

:: Permanganate

Experience in live applications has shown that for the aromatics, for example benzene and phenol, concentration changes as small as 10 ppb are detectable with high selectivity and reproducibility using s::can´s high-resolution UV instrument. Other substances with similarly strong absorption signals (molar extinction coefficient e > 10^4) allow for similar results comparable to Benzene after calibration.
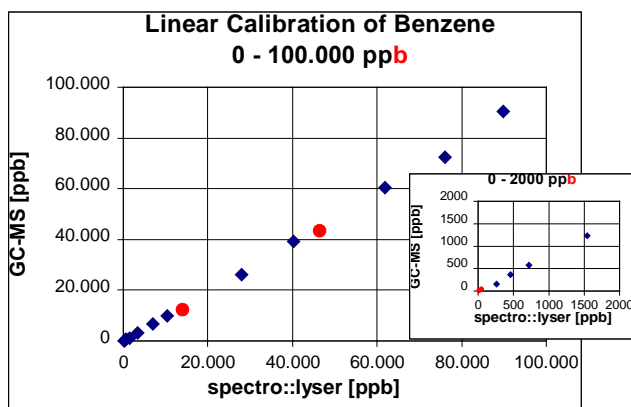

Figure 14: Figure 6: Linear calibration of benzene

Case study - Reduction of losses by the use of an s::can spectrometer probe

Brewery Göss

The target from the brewery Göss was to find a monitoring system which could reliable determine COD in their waste water, to identify if any beer extract is leaking into to waste water and be able to reduce the extract losses. The problem of leakage into the waste water exists in many industries - also in the brewery Göss. There are many possible causes for this, as for example leaking valves or gates that do not close properly. By using the s::can spectrometer probe, any losses can be identified quickly and because of the integration in a process control system, the individual departments can be informed immediately and measures to stop the loss can be taken.

Parameters monitored:

- **TSS**
- **COD**
- **BOD**
- **Temperature**

Facts & Figures

Company:
Brauunion Austria, Brewery Göss

Location:
Austria, Leoben

Date:
2005 - present

s::can Partner:
Eber, Handel - Wartung

Application:
Waste Water, Brewery

Key Products installed:
spectro::lyser
con::stat

Installation of the spectrometer probe at the brewery Göss

The first question that came up, was where to position the probe, so that all production areas could be monitored at once. It was found that the best site was a waste water shaft directly in front of the pre-treatment system. There the monitoring system is easily accessible by the operating personnel so that maintenance works can be carried out without extra effort. In addition power and compressed-air outlets were already existent and the integration in the brewery's process control system could be done with only little additional work. The spectrometer probe has been mounted directly in the waste water shaft (see Figure 1)

For all s::can spectrometer probes, Global Calibrations are available for a large number of standardised applications. The measurements at brewery Göss started using the global calibration for brewery waste water. To further increase the measuring accuracy, a local calibration of the parameters can be conducted. For the local calibration, measurement values for varying concentrations of the substances are recorded with the s::can terminal and with the help of reference measurements in the laboratory the measurement value is adjusted to the specific waste water.

Figure 15: Installation of the spectrometer probe in the waste water shaft

After the successful calibration of COD in the brewery Göss, it was tried to measure different types of beer in the water.

Measurement of beer in the waste water

Beer leaves a unique absorption curve in the water. By filtering out the specific peaks of the absorption curve in the range between 220 and 720 nm it was then possible to identify beer in the waste water. After measuring different types of beer, it became clear, that every beer is different but still there are similarities at individual wave lengths.

As a zero point for the monitoring the waste water of the brewery in its "cleanest" state was used. Because the brewery Göss produces multiple different types of beer all products were mixed in the same ratio and then step by step added to the waste water. At every step the absorption curve of the beer/waste water mixture was saved in separate file at the con::stat terminal. After the completion of the analysis the individual absorption curves were assigned to the different percentages of beer in the water and the local calibration was generated.

The last step in the installation of the monitoring station was the combination of the spectrometer probe with a flow meter. As there are temperature changes and coarse materials in the waste water, the water level is measured with a contact-free radar.

Using an overflow weir and a Q/h curve stored in the probe, the quantity of waste water was calculated and the data was feed into the process control system. By combining the parameters - like for example COD and water quantity - it became possible to calculate how much beer was leaking into the waste water.

Figure 16: Measuring principle of the spectro:.lyser

Operation and maintenance costs

The costs for operation and maintenance of the s::can probe are very low. For the ongoing cleaning the probe is equipped with an automatic compressed air cleaning which cleans the measuring path in preset intervals before the measurement. Besides the automatic cleaning some manual cleaning in regular time spans is still required, but this takes only a few minutes every week.

Resume

The s::can monitoring system is operated in the brewery Göss since September 2005 and has since the beginning delivered excellent measurement results (reproducibility of the spectrometer results in comparison with laboratory results for COD, correlation coefficient with R^2 0,9)

In October 2007 another s::can monitoring system was installed at the brewery's pre-treatment site. This system monitors the pre-treatment process. The goal was to optimize the pre-treatment and to reduce the effort and costs for the daily testing.
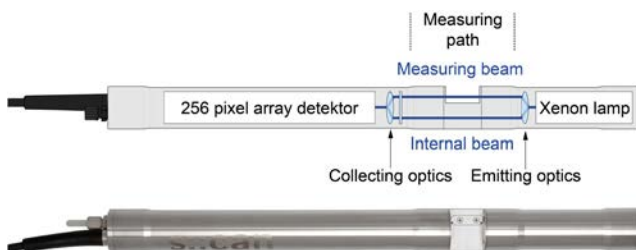
Case study - spectro::lyser in cooling water application

Formosa Plastics Group

Formosa Plastics Group's Sixth Naphtha Cracker Plant (6-NCP) includes several refinery plants. In the Sulfur Recovery Units of the plants amine liquid is used. When corrosion of heat-exchanger pipeline occurs, amine liquid leaks into cooling water To detect such events the water needs to be monitored. In 2009 Formosa Plastics Group decided to replace the old analyzers with s::can spectro::lyser. The spectro::lyser proved to successfully detected leakage of amine liquid and the customer was so confident with the performance that it was decided to replace all the existing TOC and oil-in-water analyzers with spectro::lysers.

Figure 17: Panorama view of the Sixth Naphtha Cracking Plant

Parameter

monitored:

• **TOC**

Facts & Figures

Company:
Formosa Plastics Group

Location:
Taiwan

Date:
2009 - present

Application:
Cooling Water Monitoring

s::can Partner:
Grand Tech Co., Ltd.

Key Product installed:
spectro::lyser

Challenge

Formosa Plastics Group's Sixth Naphtha Cracker Plant (6-NCP) includes several refinery plants. Each refinery plant has several Sulfur Recovery Units (SRU) that amine liquid is used. Amine liquid contains hydrocarbons coming from refinery process units. When corrosion of heat-exchanger pipeline occurs, amine liquid leaks into cooling water, which concentration of TOC and hydrocarbons increase.

In order to effectively detect leakage of amine liquid, Refinery Plant number 1 installed a TOC analyzer and an oil-in-water analyzer at the cooling water outlet of the heat exchanger. The existing

TOC & oil-in-water analyzers were old and couldn't effectively detect leakage of amine liquid.

Solution

The Customer decided to replace the old analyzers with s::can spectro::lyser in 2009. An optical pathlength of 35 mm was chosen because the monitoring range of TOC was 0 to 20 mg/l.

Evaluation

Abnormality occurred at the monitoring point soon after installation of the spectrometer probe, and spectro::lyser successfully detected increase of TOC in

cooling water caused by leakage of amine liquid. There are four monitoring points of leakage detection in Refinery Plant no. 1. Customer was very confident of the performance of spectro::lyser and decided to replace all the existing TOC and oil-in-water analyzers with spectro::lyser. Three of the four monitoring points have been monitored by spectro::lyser now.

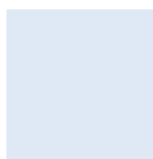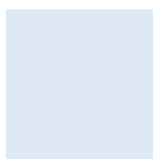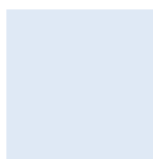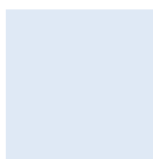The sampling point is at the cooling water outlet of the heat exchanger.

Figure 18: Sampling point at the end of the cooling water outlet

The measurement performance of spectro::lyser is highly valued by the end-user department. And maintenance team is also satisfied with the reagent-free and spare-parts-free operation of the spectrometer probe. Not only the maintenance work is simple, but the operation cost is low.

Figure 19: Flow-through installation of spectro::lyser probe inside the housing