# CLEEN WP 4.1.2.

# ON-LINE TECHNIQUES FOR WATER QUALITY MEASUREMENT

Monitoring and control of water quality is important as the increased urbanization and industrialization causes a dramatic increase of water pollution. Continuous monitoring of rivers and industrial effluents requires measuring systems that provide reliable results rapidly.

Occasional sampling and analysis can be lower in cost than online monitoring. However, the main disadvantages are that a pollution incident could go undetected between sampling times and infrequent data does not support process optimisation.

In online analysis, sampling and sample preparation are at least as important as the analyzer itself. Online analyzers should run continuously long period of times without any operation intervention. They must also be capable of maintaining their calibration status for length periods and have acceptable low maintenance costs. The analyzers must be resistant to biofouling, signal drift and blockages. In addition the analytical performance must not be significantly affected by matrix interferences.

In this report the measurement techniques of the commercial online analyzers are presented based on information obtained from the brochures of the devices and articles/reports written of the subject.

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# CONTENT

## ELECTROCHEMICAL SENSORS

Electrochemical sensors are the largest and the oldest group of chemical sensors. The modes of the measurements are potentiometric sensors (which measure voltage), amperometric sensors (which measure current) and conductiometric sensors (which measure conductivity). Electrochemisty implies the transfer of charge from the electrode to another phase, which can be solid or liquid. During this process, chemical changes take plase at the electrodes and the charge is conducted through the bulk of the sample. Both the electrode reactions and/or the charge transport can be chemically modulated, and can serve the basis of the sensing process. (Janata 2009)

An electrochemical sensor used for measuring pH, ORP (=redox), or other specific ion ($Ag^+$, $Na^+$, $CN^-$, $Ca2^+$, $Cl^-$, $S^-$, $Br^+$, $K^+$) concentrations is typically comprised of three parts: a sensing ion electrode, a reference cell, and an amplifier that translates signal into useable information that can be read. (Teledyne Analytical Instruments)

Amperometric probe with selective membrane for free chlorine, chlorine dioxide and ozone sensors for on-line monitoring of drinking and cooling water. There are no chemicals used for measurement, maintenance requirements are minimal and response time short. A programmable acidification unit can be used for sample pH adjustment or for cleaning. (HACH Lange)

The stability and reliability of the conductometric measurement is further enhanced by the Sievers membrane technology which utilizes a gas-permeable membrane that selectively passes only the CO2 produced from the oxidation of organics. By preventing compounds such as acids, bases, and halogenated compounds from interfering with the measurement of CO2 from oxidation, the Membrane Conductometric Method delivers unmatched sensitivity, selectivity, stability, accuracy, and precision. (GE Analytical Instruments)

## ***Ion Selective Electrode (ISE)***

Ion-sensitive probes are based on the potentiometric measurement principle. The probe includes at least two electrodes, a reference and a measurement electrode. The measurement electrode is equipped with a special membrane, capable of binding specific ions reversibly. Depending on the activity of the measured ions in the liquid, a varying number of ions will bind to the measurement electrode – resulting in a varying potential difference between the measurement electrode and the reference electrode, which shows a constant potential in reference to the medium. The measured potential is put in relation to the activity of the measured ion by means of a calibration function. For wastewater and surface water a lifespan of 2-3 and 6 months can be expected, respectively. Drift of the measurement signal has to be compensated by periodic calibration. Also a visual check of the probe and if necessary, manual cleaning of the probe is needed before any calibration. (Winkler 2004)

ISE electrode consist of a thin membrane across which only the intended ion can be transported. This membrane can be prepared as:
Solid membrane (e.g. glass membrane or crystal membrane) The best known example of this type of electrodes is the glass electrode (pH electrode). The example of an another glass-membrane electrode is the sodium-selective electrode (pNa electrode). Other types of membranes with fixed sites include single crystals of sparsely soluble salt and heterogeneous membranes in which the insoluble salt is incorporated in some suitable inert binder. Sensors for the detection of $Ag^+$, $Cu^{2+}$, $Cd^{2+}$, $Pb^{2+}$, $S^{2-}$, $F^-$, $Br^-$, $I^-$, $SCN^-$ and $CN^-$ ions can be constructed from such membranes.
Liquid membrane (based on e.g. classical ion-exchanger, neutral or charged carrier) The main component of electroactive membrane is neutral or charged compound, which is able to complex ions reversibly and to transfer them through an organic membrane by carrier translocation.
Compound (gas-sensing or enzyme electrode). Typically such a membrane contains an analyte-selective component which is responsible for the recognition process. These electrodes are based on the measurement of local ion-cativity variation, caused by permeation of gas molecules

(through a hydrophobic gas-permeable membrane) to the inner electrode compartment and their subsequent interaction with an internal solution. (http://csrg.ch.pw.edu.pl/tutorials/ise/ )

ISEs are commonly employed as online sensors due to their speed and simplicity, as well as low maintenance and purchase costs. Data obtained from online ISE measurements is usually semi-quantitative in nature because the analytical signal of ISE is known to be affected by matrix interferences, drift, contamination, nonlinear responses at the lower end of detection, and temperature in non-ideal measurement conditions. ISE must be regularly calibrated with standards and samples should be analyzed according to prescribed measurement conditions. (O´Halloran et.al. 2009)

ISE-sensors have proven to be applicable for many applications within water quality monitoring. In case a high trueness is required automatic compensation of the main disturbance-ion is recommended; for effluent monitoring it can be considered mandatory since the noise due to disturbance-ions can be in the range of the signal from measurement-ions. (Winkler 2004)

A very common method of measuring specific ions in solution taking advantage of the Nernst equation. Care must be taken due to interferences, temperature/matrix effects and drift of electrodes when using conventional ISE data. Metrohm Applikon B.V. uses the patented Dynamic Standard Addition (DSA) method to remove all inaccuracies. Among the long list of applications are: Sodium in high purity water, Potassium, Nitrate, Fluoride and Ammonia. (Applikon Analytical)

ISE probes are ion-selective multi-parameter probes that can measure multiple water quality parameters continuously (on-line) and directly in the water without the need for complex and maintenance intensive sample pre-treatment. ISE probes can be operated according to the „plug & measure“ principle. With a simple plug connection, which provides power supply and data communication. The sensors are connected to a terminal and are ready for use. All ISE probes are pre-calibrated. (s::can)

## OXIDATION

Organic carbon compounds are converted to $CO_2$, which is then measured using a non-dispersive infrared detector. There are several possible oxidation methods, each designed for a specific type of water or use. The oxidation systems used in commercial on-line systems are 'low temperature' (under 100 °C) or 'high temperature' (680 – 900 °C, or higher) methods and chemical oxidation systems which use different oxidizing reagents and are catalyzed by UV lamp and/or heat.

Sample is drawn into the devise by the source pump, and continuously sampled by a feed pump to a scrubbing column, where dilute acid converts inorganic carbon compounds to $CO_2$ which is removed by sparging. The sample is pumped to reactor where organic carbon compound are oxidised. The $CO_2$ is measured by a non-dispersive infrared detector (NDIR). (HACH)

### *Chemical oxidation*

Wet-chemical oxidation conform with ISO 6060 for dichromate method (K2Cr2O7) and with ISO 8467 for Permanganate Index (KMnO4). The standard 2 hours oxidation time can be reduced to 20 minutes by means of a special digestion unit. (Applikon analytical)

Aromatics and pyridines are not oxidised at all. In natural waters these interferants are rare, but care must be taken with industrial liquors. Sample must be pretreated to avoid blockage, this may be achieved with a cutter pump and a crossflow filter. Soluble COD may be determined using a submersible ultrafilter. (Envitech)

Excellent TOC accuracy from low parts-per-million to moderate concentrations of salt-free samples. Minimum maintenance. Preferred method for most applications. (Teledyne Analytical Instruments)

The UV-heated persulphate method assures full compliance with international standard methods. Hot UV / persulfate method allows true continuous measurements. Outstanding reliability and accuracy thanks to the use of first class and robust wet-part components: low-speed peristaltic pumps, oxidation reactor and robust auto-zeroing IR detector. (Applitek)

Ozone/Hydroxyl radical method is excellent for low to high levels of TOC analysis for difficult to oxidize samples or in undiluted acids or industrial salts over 26%. Low maintenance. Preferred substitute for High Temperature Combustion in most applications. (Teledyne Analytical Instruments)

### *Thermal combustion*

Conventional thermal catalytic oxydation methods use temperatures between 680 °C – 1000 °C. Thermal combustion is preferred for some higher range samples which have limited oxidation efficiency by other methods. High temperature combustion has been engineered to work without the aid of expensive catalysts by using temperatures of more than 1200 °C. Therefore, difficult to combust compounds are oxidised effectively and rapidly, regardless of their composition. (Lar Process Analysers AG, Teledyne Analytical Instruments).

The calibration and validation of the TOC analysis calibration function for measurement ranges of 0-2.000 µg/l, is usually a very difficult task for the operator. Using the newly developed „gas calibration“, a patent pending method from LAR, this procedure has been significantly simplified. QuickTOC®condensate works without the usual contamination risk and has no need for a calibration solution. Even within the lowest measuring ranges the calibration can easily be performed with the calibration gas and afterwards also verified with it. (Lar Process Analysers AG)

### *Supercritical Water Oxidation*

GE Analytical Instruments' patent-pending Supercritical Water Oxidation (SCWO) technique enables to achieve its superior analytical performance and unsurpassed calibration stability. Using an oxidation process in a supercritical state has shown superior TOC recoveries across a broad range of organic compounds and particulate impurities. The technique brings water to a supercritical state by heating a water sample inside a sealed reactor module to 375 degrees C and raising the pressure to 3200 psi. Under these conditions, water is neither a gas nor a liquid, but exhibits beneficial properties of both. SCWO allows the InnovOx to achieve greater than 99% efficient oxidation — regardless of organic compounds and impurities in the water. The result is greater TOC measurement accuracy and precision. This new process removes all oxidation byproducts and sample contamination between each analytical run, eliminating frequent maintenance and expensive parts replacements providing reliable, long-term system performance. (GE Analytical Instruments)

## OPTICAL TECNIQUES

### *Nephelometry – light scattering*

The word "nephelometric" describes an optical principle of instrumentation whereby turbidity is determined by measuring the amount of light scattered at some angle (usually 90 degrees) from the incident light path by particles suspended in the test solution. (Hach C. 2003)

Continuously flowing sample flows through the patented bubble removal system, which vets entrained air from the sample stream and eliminates the most significant interferences in low level turbidity measurement. Photocell detects light scattered at 90° from the incident beam. The measurement is not affected by variations in flow and pressure. Calibration or verifying the performance takes less than one minute. Cost effective, one-time instrument. No consumables are needed. (HACH COMPANY)

The turbidity analyzer from datalink instruments uses an Infrared light source that makes it not sensitive to water color. It is well suited for low turbidity application as well as rough industrial effluents. (datalink instruments)

### *Colorimetric measurement*

Colorimetric measurements are largely based on direct adaptations of standard method which use reagents to obtain desired complex ion formation to quantify the concentration at a specific wavelength. They require regular calibration with standard reagents. (O´Halloran et.al. 2009)

Predominantly used in water quality analysis and plating solutions. A technique that is very useful for low concentrations of analytes. Using Differential Absorbance Colorimetry (DAC) the effect of background sample colour and turbidity is removed. The wide range of LED sources and filters makes it possible to offer a solution to a wide range of applications. Typical examples are COD measurements, Ammonia and Chlorine in waste /drinking water, Silica and Phosphate in boiler feed water, Iron in many different waters, Phenol in industrial waste Water, calcium and magnesium in Brine. (Applikon Analytical B.V.)

A pump controls the volume of incoming samples and reagents (indicator and buffer). A zero reference point is established with the first sample in the cycle by measuring blank absorbance. Indicator and buffer are added. Colorimeter measures the light transmitted through the sample and the color intensity is compared to a reference standard. The sample cell is flushed with new sample and the cycle can repeat itselt every 2.5 minute. (HACH)

### *UV and UV/VIS spectroscopy*

The measurement principle in UV spectroscopy is based on the specific absorption at the specified wavelength or wavelength range in the ultraviolet spectra. They require conventional calibration with standard reagents. The method usually employ pattern recognition techniques to quantify the absorption profile. They are employed mainly because samples can be analyzed with very little sample preparation, no chemicals are required and they have low operational costs. Such method have been developed for monitoring Chemical Oxygen Demand (COD), Total Organic Carbon (TOC), Biochemical Oxygen Demand (BOD), Nitrate and Chromium VI. (O´Halloran et.al. 2009)

Monitoring at UV 254 nm is used for effluent discharge monitoring to detect biological or organic components, as surrogate for BOD/COD/TOC. The key features are: almost instant response, continous on-line operation, no need for reagents, automatic cleaning, flow through cell, sample flow detection and alarm relays. The UV-0254 provides a measurement of light absorbance that can be correlated with soluble COD after compensating for turbidity at a second wavelength.

A multi-parameter analyzer combines high precision UV transmission measurements with a mathemathical spectral analysis software in order to provide single substance concentrations from natural or artificial mixed samples. The system can determine simultaneously and online NO3, NO2, TOCeq, CODeq or many others parameters without chemical reagents.

UV spectroscopy measuring principle requires no chemical reagent or calibration solutions resulting in very low operation and maintenance costs. The probe can be directly put in water, no pumping or filtration system is required. An optical turbidity compensation maintains correct measurements.

On-line chromium VI analysis has become essential to uphold the environmental and sanitary regulations for all kind of water: rivers and underground water, drinking water, industrial effluent and sewage. Reliability and stability are the main requirements of on-line analysis system achieved by UV spectroscopy. (Metex corporation )

Manufactures e.g. datalink instruments, Envitech, HF Scientific, Metex corporation, s::can, TriOS.

### *UV/VIS fluorescence*

Real-time fluorescence data have mostly been obtained for seawater with instruments specifically designed for this application. Few continous real-time fluorescence experiments have been performed on freshwater, mostly due to the lack of proper instrumentation. One limitation was the clogging of pre-filters which require frequent filter replacement. Carstea et al. have published an experiment on using in-situ fibre-optic probe to obtain fluorescent data for two weeks. Apart

from increased obserbations of biofilm fragments, as well as a graduate increase in pH, no major problems were wncountered until a power supply failure. (Carstea et al. 2010)
A wide range of applications can be covered depending on the optical head used. Using high sensitivity photomultiplier very low concentration in the ppb range can be measured. Main applications are measurement of chlorophyll A, PAH (polyaromatic hydrocarbons) and fluorescent traces in rivers/lakes/reservoir systems/drinking water. No Chemical reagents or calibration solutions is needed and so the operating and maintenance costs are low. (datalink-instruments)

The UV fluorescence principle, used for detection, is much more sensitive than any other existing detection principle, like infrared scattering, etc. This allows the detection of very low levels of PAH (single ppb levels) for use in drinking water or condensate applications. A new innovative coating on the lenses helps prevent the optics from fouling. (Envitech)

microFlu-blue is a low-cost miniaturized submersible fluorometer for high precision and selective phycocyanin fluorescence measurements in cyanobacteria. The combination of a miniaturized design with long-term stability makes it suitable for blue algae monitoring applications in lakes and rivers as well as for all applications in the field of water quality and waste water monitoring. Internal reference measurement of the emitted light compensates aging and temperature dependences of the high-efficient LEDs, used for fluorescence excitation. (TriOS)

### *Luminescence*

Sensor is coated with a luminescent material. Blue light for an LED is transmitted to the sensor surface. The blue light excites the luminescent material. As the material relaxes it emits red light. The time for the red light to be emitted is measured. Between the flashes of blue light, a red LED is flashed on the sensor and used as internal reference. Increased oxygen in the sample decreases the time it takes for the red light to be emitted. Time time measurements correlate to the oxygen concentration. The sensor is unaffected by pH swings, hydrogen sulfide, wastewater chemicals, heavy metals, or organic build-up on the sensor. Sensors using luminescence include some turbidity sensors as well as some new type of Dissolved Ozygen (DO) sensor which employs a

Light Emitting Diode (LED) to measure DO concentration instead of using a conventional membrane based sensor. Unlike electrochemical dissolved oxygen sensor technologies, the Luminescent Dissolved Oxygen (LDO) sensor does not consume oxygen.

The sensor does not use replaceable membranes or cartridges. Because there is no anode that is oxidizing, the sensor does not require frequent recalibration or frequent cleaning, resulting in longer sensor life and more stable and accurate readings. The system is also flow-independent so measurements can be made in applications with low or no flow. Inert construction will not corrode in high salinity samples. Insensitive to common interferences such as hydrogen sulfide, chloride, chlorine, ammonium, and many others. (Envitech Ltd, HF scientific, HACH COMPANY)

### *Remote sensing*

The use of satellite remote sensing enables efficient monitoring of spatial water quality variation in lakes and coastal waters. Best results are obtained by combining remote sensing with the results of conventional monitoring, which is based on water sampling at fixed stations. The development of the interpretation algorithms requires also detailed measurement of optical properties of water. Images from remote sensing satellites are used in the estimation of turbidity, total suspended solids, surface accumulation of algal bloom, humic substances, chlorophyll a and Secchi disk for Finnish coastal waters and lakes. (Kallio et al. 2009)

RAMSES-ARC is a stand-alone highly integrated hyperspectral radiometer for the UV and/or VIS spectral range. Small size and very low power consumption make it suitable for hand-held and autonomous applications. Features: low power consumption, small sized, wide range of applications in a wide range of environmental conditions (from the equator to the poles), high precision, modular system, newest technology with nanocoating. Applications are e.g. monitoring, water quality, field measurements and satellite data validation. (TriOS)

## LAB-ON-CHIP

Capillary electrophoresis (CE) is considered to be a very promising technology for on-line analysis and monitoring purposes. CE is a technique for separation and measurement of organic and inorganic ions. In the microchip CE approach, the glass capillary is replaced with microchannels. Electrodes are connected to each end of each channel, giving a sum of four electrodes. The resulting measurement is shown in the form of electropherogram that presents the detector signal versus time plot. Each signal peak represent a different ion. A sufficient high degree of automation is needed in order to enable measurement platform in process monitoring. One major current activity is the technological development of automation sampling and sample pre-treatment steps. Capilix is implementing refrective index sensing on-chip by further development of their integrated optics technology. (Capilix)

## CONCLUSIONS

There is no broadly agreed international standards or methods developed that allow for large-scale, online, reliable and cost –effective data to be acquired, integrated and applied. This is primarily due to the maintenance and calibration costs associated with the instrumentation as most online analysers are based on direct adaptations of traditional laboratory-based methods. There are significant economic and logistics costs associated with maintaining online analysers, especially in remote areas, due to maintenance, calibration, blockages, matrix interferences, biofouling, signal drift and reagent consumption. (O´Halloran et.al. 2009)

Some online methods are based on electrochemical detection with specific emphasis on voltametric and amperometric techniques, as well as Ion-Selective Electrodes (ISE). Other online monitoring systems are based on optical detection techniques such as UV absorption with the majority employing colorimetric detection principles. (O´Halloran et.al. 2009). A strong input in electrochemical sensor technology can be expected from improved electronic equipment so that lab methods such as cyclo-voltametry and impedimetry can be applied in field measurements. (Guth et. al. 2009)

The great success of optical-fiber sensors is because they can be used to tackle difficult measurement situations where use of conventional sensors is not appropriate. The sensors are usually compact and lightweight, minimally invasive, and can be multiplexed effectively on a single fiber network. They are immune to electromagnetic interference, because there are no electrical current flowing at the sensing point. (Marazuela 2002). Optical sensors are cost-effective devices or enable rather sophisticated multisensory applications. Because of the existence of many different optical principles which can be classified into use of direct optical detection or taking advantage of labeled compound, in principle many of these methods can be applied to a huge number of applications. (Gaulitz 2005)

The quality of sensors does not just depend on transduction principles but on the total sensor system defined by this transduction, the sensitive layer, data acquisition electronics and evaluation software. It is becoming evident that of the different sensor principles – electronic, electrochemical, mass-sensitive, or optical devices – none is generally superior, but rather the feasibility depends on the application. (Gaulitz 2005)

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