

On line analysis of organic in water

For years TOC analysis has been reserved for specialists. Now it is becoming more and more frequently used for water quality control.

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Introduction

On line chemical analysis has been developed significantly thanks to digital electronics' use of microprocessors together with the application of sophisticated and accurate analytical techniques.

The result of this combination is readily available technology which allows for on line performance of almost any analytical determination for quality control which is normally made in a laboratory. Moreover it allows for the automation of traditional chemical analyses generally considered difficult to do if not manually.

Correct monitoring can only be obtained utilizing sophisticated and modular instrumentation (with capacities of auto-diagnostics, auto-calibration, alarms) which can be easily and efficaciously maintained and repaired.

It is important not to forget the collateral aspects of analysis, i.e. proper sampling and preconditioning of the sample as well as proper data collection.

It is also very important that technicians are available for maintenance and control of the operation of the analytical system .

Nutrients in water

In water analyzed for environmental purposes such as industrial, civil, surface (rivers, lakes, seas) waters, some very important substances can be verified; namely nutritious matter or nutrients.

These are: **organic substances**, **nitrogen** compounds (ammonia, nitrates, nitrites) and **phosphor** (total phosphor or orthophosphate). These substances are called **nutrients** because they promote the growth and development of several types of microorganisms which are present in water.

In waste water treatment plants, nutrients are fundamental because they assure the greatest growth of microorganisms and consequently the best aerobic and anaerobic treatment

The ideal amount of nutrients in waste waters is normally considered to be the ratio of

carbon: nitrogen: phosphor = 100:5:1.

The lack of nutrients in waste water, particularly in industrial waters, together with other factors (pH, low dissolved oxygen levels) may promote the growth of

undesirable microorganisms which cause plant inefficiency (thready microorganism growth - sphaerotilus, leptotrix, beggiatoa; mold which causes sludge explosion).

The presence of nutrients in surface waters also causes algae growth which diminishes dissolved oxygen.

The river therefore becomes poor in oxygen and consequently in animal life.

Nutrient control is becoming more and more fundamental to treatment plants' ability to manage and limit pollution.

Organic material

The total amount of organic matter in water is called the "**organic load**" and by definition consists of chemical compounds containing carbon atoms (aliphatic and aromatic hydrocarbons and all of their derivatives, solvents included).

Inorganic compounds which contain carbon atoms *are not* part of organic load; for example carbon dioxide (CO₂) dissolved in water produces carbonic acid (H₂CO₃) and its salts which are widespread in nature (sodium, calcium and iron salts).

Other chemicals that *are not* part of the organic load are: monoxide (CO), bisulfide (CS), carbon tetrachlo-

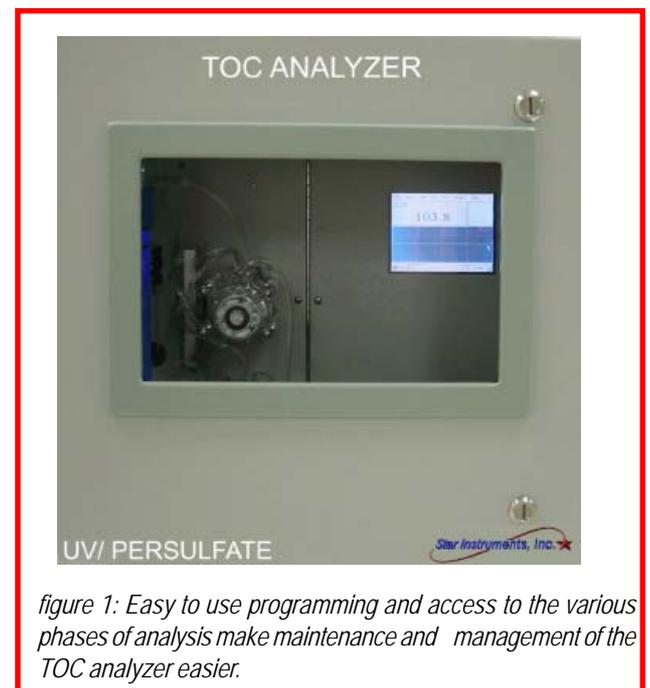


figure 1: Easy to use programming and access to the various phases of analysis make maintenance and management of the TOC analyzer easier.

ride (CCl_4), cyanide, thiocyanate, carbide and pure, amorphous and crystalline carbon.

Organic compounds are biodegradable, that is they are used as food by various types of microorganisms such as bacteria and molds; these microorganisms digest organic matter and transform it into carbon dioxide and other simpler compounds.

In doing so they produce substances necessary to their growth and energy for vital processes.

This digestion process is called "decay" or "putrefaction" and it occurs along with dissolved oxygen consumption.

Dissolved oxygen concentration decreases and the water becomes putrid.

No oxygen remains until the biologic matter collapses.

Organic matter is naturally present in surface water (fresh and sea water).

Its presence may also be due to intentional spilling by industries or communities (industrial or civil discharges), accidental spilling (cooling waters and condensates), or inefficiency of water purifying systems (ultrapure water for the electronic or pharmaceutical industries).

Organic matter pollution is the most common type of water pollution. The presence of organic matter (which is not foreseen or accidental) is an indication of anomalies in water.

Methods of Analysis for Organics

In past years different types of analytical methods have been used for the determination of organic load.

The best known methods are **BOD**, **COD** and **TOC**. Regulations and guidelines for these types of analysis have been established.

For practical use other methods have been employed such as **TOD** (Total Oxygen Demand), **Kubel index** (permanganate oxidability) and many other indirect methods.

All of them are potentially valid, but too specific for particular uses with single applications.

They are therefore not suitable for precise and reliable general use.

Most common of the above-mentioned methods are:

BOD (Biochemical Oxygen Demand) and **COD (Chemical Oxygen Demand)**; these are both indirect methods based on oxygen consumption measurements made during the biologic oxidation reaction.

Oxygen consumption is relative to organic matter concentration.

Comparison between COD and TOC

COD analysis has been used for decades and it is therefore considered "official" for all research, calculations and daily use with discharge management. For

this reason it is necessary to constantly refer to COD.

Officially the **COD** name is only related to the analysis performed exactly following the official methods: digestions for 2 hours at given conditions, and with specified chemical, and determination of the reduced Cr VI to Cr III by colorimetry or Redox titration.

Any other analytical methods performing an oxidation in a different form cannot be called properly COD.

Some problems are (assuming the analysis is done correctly):

- time necessary to perform this analysis (approx. two hours),
- interference which makes the test inaccurate,
- restricted measurement ranges (i.e. ranges lower than 20 ppm and higher than 1000 ppm are out of the question)
- reagents which are considered dangerous and toxic (highly acid solutions containing mercury salts).

COD values are, at any rate, *comparable* to TOC values.

With both methods organic matter oxidizes according to the following equation:



One carbon atom (P.A. = 12) is combined with two oxygen atoms (P.A. = 16) i.e. 32 grams of oxygen are used for 12 grams of carbon.

Ratio should be $\text{COD}/\text{TOC} = 32/12 = 2,666$.

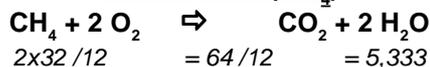
This value is theoretic and varies for organic matter because hydrocarbons, which contain numerous hydrogen atoms, are able to combine with oxygen and thus produce water. These compounds require a greater quantity of oxygen, corresponding to a larger COD value.

Other compounds have oxygen atoms which take part in the reaction thereby lowering the request for external oxygen. A general indication of the COD/TOC ratio is presumed to be around 3. Different values indicate a change in the organic load.

It has been noted that the COD/TOC ratio in plant dis-

Examples:

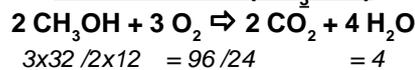
METHANE (CH_4)



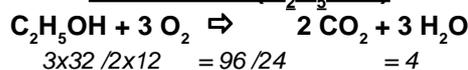
BENZENE (C_6H_6)



METHANOL ($\text{CH}_3\text{-OH}$)



ETHANOL ($\text{C}_2\text{H}_5\text{-OH}$)



TOLUOL ($\text{C}_6\text{H}_5\text{-CH}_3$)



charge is well defined and repeatable, as long as the organic matter type is constant.

It is clear that this ratio can change depending on the oxidation state of the organic matter. It is obvious that Inlet water of a treatment plant has a COD/TOC ratio which is different from that of the outlet water (after treatment). Nevertheless each single ratio remains more or less constant.

Various tables are available (see next articles), which have been completed by different industries (petrochemical, pharmaceutical, food, cosmetic, chemical etc.); these tables verify the consistency of the ratio.

In the case COD on line analysis is absolutely necessary, it would be possible to automate utilizing analytical robots belonging to the same category as those dedicated to nutrient analysis.

TOC analysis

All methods cited in previous paragraphs provide indications of organic matter concentrations in relation to oxygen consumption. Those are indirect method.

On the contrary, the analytical method which is employed for organic carbon analysis, TOC, implies the **direct determination** of the amount of organics through measurement of carbon in CO₂ molecules generated during organic matter oxidation.

This method is as a result based on organic matter oxidation followed by CO₂ determination.

To avoid possible interference, inorganic carbon is removed by means of acidification and stripping.

Over the years and since 1962 when the first TOC analyzer was presented in the United States by Dow Chemical and Union Carbide, different types of analytical methods have been developed and relative instruments have been invented - both laboratory and on line; all of these instruments were designed to employ available technology of the day to perform this analysis.

Various institutes and standardization offices approved and documented official methods for TOC analysis (Standard Methods 5310A, B, C; EPA 415.1 and EPA 415.2; APHA 505a e B; ISO 8245; DIN 38409H3; ASTM; UNICHIM 944).

Between 1995 and 1997 the CEN/TC technical committees met to discuss "Water Analysis" and "Water Quality". Those meeting was arranged by the European Committee for Standardization.

TOC analysis in water, after the evaluation by European experts of years of research and experience, was proposed for official approval as a "Guide Line".

It was later recommended to all European countries and CEN members as an official analysis for the purpose of water quality control.

The draft have been approved in 1997 and become an European Standard

Definitions

Definitions concerning organic matter analysis are varied, although efforts at normalization have been made, a unequivocal and universal definition does not yet exist.

Some examples of common abbreviations:

TC = Total Carbon;

TIC = Total Inorganic Carbon;

IC = Inorganic Carbon;

TOC = Total Organic Carbon;

DOC = Dissolved Organic Carbon;

NPOC= Non Purging Organic Carbon;

NDOC= Non Dissolved Organic Carbon.

In some cases "Totally Organically bound Carbon" is considered correct.

On line TOC analysis for water and pollution control

Process TOC analyzers are assembled according to the official criteria mentioned above.

The STAR TOC for example is the result of extensive experience of several European and American companies. Together they developed an instrument which draws on individual experiences had with installation and utilization of a great number of different types of on line analyzers.

The STAR TOC operating scheme and its analytical functions can be summarized as follows:

- Sample extraction and pretreatment
- Inorganic Carbon purging
- Organic matter oxidation
- Separation of liquid and gas phases
- Survey and measurement of the CO₂ produced
- Analytic output processing
- Control, calibration, cleaning, and service of various parts of the analyzer

When manufacturing this TOC analyzer, research done in the last few years (by public offices, EPA and ISO and private organizations such as the Instrument User's Association) as well as the practical experiences of users and maintenance firms have been taken into account.

In Italy, for example, the consideration after technical assistance given during a 15 years of on line TOC analyzer distribution, made it easy to identify the areas where operation and maintenance problems normally occur, and analytical problems which correlate with the dependability of the analysis.

A "traditional" TOC analyzer required 70% more technical assistance than the instruments used for nutrient analysis (taking into account the length of operation and the same number of units)

Problems more frequently found (in decreasing order) in the process of technical intervention:

- various problems with the hydraulic system
- frequent IR calibration resulting in the need to use calibrated gases
- various problems with electrical parts
- overflow of hydraulic parts
- UV reactor breakdowns and problems
- hydraulic clogging.
- pumps and motors needing to be replaced
- IR cell corrosion
- analyzer calibration

When the decision to manufacture a new TOC on line analyzer was made, these problems were studied in depth. All available knowledge and technology was utilized in an attempt to find solutions.

To follow is an explanation of the analysis utilized by the instrument (taking its current configuration into consideration).

Sampling

The sample must be representative for the analysis and must therefore be as large as possible in for an on line analysis to be made.

The instrument was therefore equipped with suitable external devices (fast loop, autocleaning filtering system, fixed/dynamic external dilution, decantation systems) which allow it to extract the sample by means of an inner 28 ml/min. peristaltic pump.

The clogging of hydraulic parts must be avoided, however at the same time the probable filtration must not alter the sample composition and must allow for the analysis of suspended solids up to at least 100 μm as required by ISO/CEN guidelines.

The inner tube diameter is large and tapers to avoid dead points.

The analyzer is equipped with auto cleaning systems which are programmable. Little need for frequent maintenance is guaranteed by numerous sensors and alarms which identify clogging, lack of sample as well as malfunction.

In particular cases when **DOC** (Dissolved Organic Carbon) analysis is needed, and only the soluble part of the sample is called into play, external filtration systems must be used with 0.4 μm porosity.

Inorganic Carbon Removal

Inorganic carbonates are removed from the solution by acidification, which brings it to a pH value lower than 2.

Normally phosphoric acid is used for its buffering capability. In this manner all carbonates and bicarbonates are converted into CO_2 which is insoluble in an acid environment (lower than 2).

Subsequent stripping by carrier gas allows full CO_2 removal from the solution.

Since the IR analyzer used in the measuring stage, is unaffected by acid and corrosive gases there is no limit to the use of the acid type or its concentration (as that it is about 10% v/v).

Maintenance problems may occur due to the possibility of insoluble phosphate salt precipitation. Should a significant quantity of calcium be present in the water, it would be advisable to use different acid in order to avoid the precipitation of Calcium Phosphate salts.

In order to eliminate analysis problems due to the interference of carbonates which may have been incompletely removed (causing them to be revealed as TOC), the system must be appropriately configured with an anticipated inorganic IC value present in the analyzed water taken into account.

Organic matter which is volatile may be stripped together with inorganic CO_2 (they are therefore not completely determined with this system of analysis).

Oxidation of organics

There are several possible oxidation systems, which satisfy TOC regulations.

Each type is designed for a specific type of water or use.

They are generally distinguished by '**low temperature**' (under 100 °C) or '**high temperature**' (over 680 °C or 900 °C or higher) methods with other technical and instrumental differences categorized according to application or use - either laboratory or on line instruments.

For industrial waste waters , the high temperature oxidation system has most often been used, despite the fact that it presents operation problems and needs constant maintenance.

Nevertheless it is efficient and assures the best organic matter oxidation.



The oxidation reactor of this system does get dirty and clogged because of dissolved salts or suspended solids present in water.

The use of the low temperature oxidation, if properly made, leads to whole oxidation of almost all organics that may be present in the water with only few exceptions, and depending from sample matrix.

It is highly efficient; does not present maintenance or malfunction problems, so the TOC analyzer can be used continuously and for a significant amount of time.

In the analyzer described there is a chemical oxidation system based on a highly concentrated sodium persulphate, catalyzed by a double wavelength UV lamp.

This reaction occurs inside an innovatively designed reactor which guarantees the most efficiency. Reactor temperature is adjusted and maintained at 75 °C by means of electric resistance.

This system combines economic operation charges together with the best oxidation ability.

Sodium persulphate is an oxidation agent which has maximum oxidation potential ($E_{11} = - 2,012 \text{ eV}$).

It is stable for up to one month, is highly soluble and can be prepared in very concentrated solutions (1,5 M); Moreover it does not generate corrosive gases.

Low temperature oxidation can also dissolve suspended substances which oxidize at first contact with the very aggressive chemical used, thus facilitating the complete oxidation without problem.

Sodium persulphate in solution, with energy (UV and heat), generates **OH°** highly oxidant radicals. Its high concentration allows for good oxidation even in the presence of medium chloride concentrations. Chlorides actually tend in their turn to oxidize using the equivalent of the persulfate with a reaction which is kinetically faster than the oxidation of the organics.

The use of a thermoregulated reaction system (75 °C) allows one to obtain maximum oxidant power with persulphate, independent from the ambient or sample temperature, avoiding measurement variations due to temperature fluctuation. (winter and summer variations)

Employment of a special manufactured UV lamp was decided upon because of its resistance and long life - due to both quality and gas purity (Hg).

This lamp can also operate in dry conditions without fear of breakdowns or malfunction of any sort.

Double wavelength (254 and 185 nm) allows for higher oxidation power: 185 nm radiation is absorbed by oxygen, thus generating ozone. 254 radiation is absorbed by most organic matters, contributing to double link demolition; it is also absorbed by persulphate generating OH° oxidant radicals and by ozone, generating atomic oxygen which in turn is oxidant.

At the site of oxidation, particular care was used with the reactor design.

In order to reduce manufacture and maintenance costs and increase, if possible, oxidative efficiency, the 'ideal' UV reactor design was developed.

The reactor can be disassembled quickly and opened - thus making maintenance easy.

It has no dead points where solids or crystals might build up and has no delicate washers which could lead to leaks.

Its inner structural design (patented) generates a vaporized mixture of sample, carrier gas and persulphate.

This mixture offers a wide surface for UV radiation and promotes total oxidation. Surface and contact times for

such a mixture utilizing UV radiation of single lamp (length 15") are superior to those of similar multilamp systems.

This is thanks to an inner design in which the sample, in the form of aerosol, follows a helicoidal multistage path before leaving the reactor.

figure 4:

High Precision Non-Dispersive IR detector - stabile and highly resistant to Wet and Corrosive Gases

The system is also protected from malfunction by sensors which interrupt the sample and gas flow in the event of clogging, crystallization, or sample loss.

This oxidation system guarantees highest efficiency and savings on maintenance costs thanks to quality control of compounds as well as technical precautions.

The carrier gas is compressed air which flows through a physical purification system and undergoes a CO₂ removal process.

This system is cheap, does not require maintenance and avoids the need to use compressed oxygen bottles.

CO₂ Detection

The CO₂ detection and oxidation systems are the most important components of a modern TOC analyzer.

The CO₂ detector must not be fragile, easy to get dirty, or interfered with by water steams or gases.

Moreover the drawing and oxidation system, in order to avoid malfunction, must not be sub-dimensioned..

For this reason some instruments are present in the market which use fragile and critical IR detectors analyzers and must analyze a lower amount of water, use less acid in the IC removal stage (to avoid acid steams) and use a much less concentrated persulphate salts (in order to avoid acid steams). The cell windows of some Luft type detector are made in CaF₂ and the inside cell body (typically gold plated) may be damaged by corrosive gases (humid and acid) which also may carry over particulate.

For an IR to be of good quality, an anticorrosion sys-



tem is not enough. It must be very sensitive, long lasting, without drifts and must provide excellent linear output for the entire measuring range.

The IR detector installed in the STAR TOC analyzer was developed because of high precision, sensitivity, stability and lack of drift. It is, moreover, easy to calibrate and will not be damaged by wet and corrosive gases.

The measuring cell, which comes into contact with the sample is made of borosilicate glass, and the optical windows are made of sapphire; there are NO moving parts and the system doesn't vibrate.

The optical part is purged by the carrier gas itself, on the basis of which the sample blank is measured, thus eliminating problems due to gas purity and CO₂ change (CO₂ present in the carrier gas itself).

The used IR wavelengths (2353 cm or 4,25 μm) are specific for CO₂ and therefore no other absorption takes place of other substances, water steam included.

Another quality to be noted apart from the consistency of measurement is the possibility it gives to avoid need for repeated calibration and technical intervention of the optical compounds.

Output Processing Analysis

Analytical output processing corresponds to the processing of signals which come from the IR and its linearization in reference to:

the selected concentration range,

signal compensation (in the case of aging sources or dirty windows).

type and quality of signal emitted,

sensitivity and speed of answer,

type and quality of measurement

alarms which warn of malfunction.

These issues will become more and more simple because of the now widespread use of microprocessors and digital techniques; moreover the configuration of the analyzers will become easier and easier.

For the analyzer a very simple, but complete, user interface was chosen.

Utilizing a large keyboard, several analytical phases are programmable from a complete intuitive menu.

It is possible to perform automatic calibrations, schedule autocleanings, assign several different alarm relays for different analytical phases (in the case for instance of loss of chemicals, hydraulic leaks, clogging, lack of carrier gas etc.).

The instrument can be properly managed when operation is interrupted due to malfunction and/or in the case of any irregularity (brought to light by alarms).

It is also useful to help insure prompt intervention and optimal maintenance.

Several TOC analyzer have been supplied equipped with an interface consisting of special software allowing the instrument to be connected to a telephone beeper. The

digital system is able to communicate, by means of an alphanumeric receiver, various messages about the type of malfunction, with the ability to select to which terminals the messages must be transmitted:

for instance "lack of chemicals" would be a message to be sent to the laboratory; "malfunctioning" would be sent to maintenance service; "measure alarm" to be sent to the process checking point, etc.

STAR TOC analyzer can also be used to determine TOC of different flows such as inlet, intermediate, outlet flows.

All of this is possible thanks to industrial computers which create *multistream* conditions.

These automated systems are also able to operate in other more "typical" ways.

They are able to acquire data from various instruments such as that regarding nutrients, pH, flow measurement, rainfall etc. Data is elaborated in database form and, if required, may be introduced into a network.

Several TOC analyzer have been also installed connected with a water sampler. The alarm originated by the TOC analyzer will trigger the sample, activating the sampling sequence at the moment of a potential pollution.

Other TOC analyzer have been connected together with a flowmeter, giving not only a absolute value of TOC concentration but a more precise and useful "load value" in order to better manage the treatment of the waste water stream.

Conclusion

Nowadays TOC analysis is widely used for water quality control, while in the past it was reserved for specialists. Applications of this analysis are requested more and more and TOC analysis is consequently becoming essential to water management. Not only water which is considered a waste product, but water as a true raw material.

American Pharmacopoeia (USP) has recently revolutionized analytical systems for ultrapure and injectable water. Since January 1996, TOC analysis (with a limit of 500 ppb) has been compulsory for all pharmaceutical waters regulated by USP.

New European guidelines being developed by the CEN/ISO committee will contribute to a higher diffusion of this method.

TOC analysis is believed to improve the control of quality and contribute to the creation of an environment with cleaner water.

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