

# Organics in Boiler Water Condensate

## WATER WASTEWATER

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With the wide use of high efficiency boilers and current high-pressure boilers in industry today limiting condensate analysis to the more traditional parameters can result in very expensive repairs.

Condensate return should be the highest quality least expensive water that most systems can generate. Boiler operators do not want to lose this or have it contaminated.

Condensate return analysis has been typically restricted to monitoring for corrosion. The most common parameters to monitor this have been pH, Conductivity, iron, copper and Ammonia. Levels of more than a few parts per billion (ppb) of metals if found in the condensate, may indicate the presence of corrosion in the boiler. Ammonia in the presence of oxygen can cause serious copper corrosion.

However, when the use of boilers extends to industries that have high levels of organic processing, such as Paper & Pulp, Petrochemical, Refining, Grain Processing and Food Processing the need to monitor other possible contaminants is required. In these industries steam is used as part of processing the product and therefore has the opportunity to come in contact with the process and become contaminated and hence the product can find its way into the condensate. If the steam contains organic contaminants then traditional condensate analysis will fail to pick it up. One of the classic on-line measurements for boiler water condensate is conductivity and though this is ideal for detecting products of corrosion, since they are ionic, it is severely limited in its ability to detect organics. With the majority of organic molecules being non-ionic they will not be detected by conductivity and therefore would provide a false positive and signal that it is ok to reuse the condensate.

Re-using condensate contaminated with organics will result in fouling of a boiler, major damage resulting in early shutdown and potential loss of production. So the financial implications of not monitoring for organic contamination are far reaching. Many large production facilities today, charge individual production units for steam consumption and they are credited for clean condensate returned to the boiler. With the addition of an organics monitor the quality of condensate returned can be accurately assessed.

### Methods for monitoring organics in boiler water condensate.

Without exception the way to monitor for organic carbon in water is Total Organic Carbon (TOC) analysis. However, there are a number of available methods on the market each having advantages and disadvantages. The remaining part of this paper will review each method outlining its advantages and disadvantages.

In boiler water condensate the concentrations of organics are low, typically in the range of 0 - 15 mg/l and are measured between the condenser and the return condensate line.

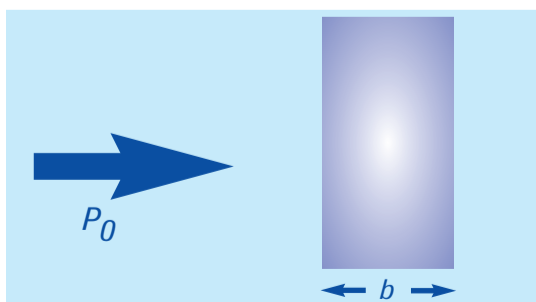
TOC analysis has been available for many years as an on-line measurement predominately using three different methods.

- Molecular Absorption UV 254 nm
- TOC Analysis using UV Persulfate.
- TOC Analysis using High Temperature Combustion.

The advantage of TOC as an analytical method is that it is not specific to any one organic molecule, but a measurement of all organics. When you investigate the three predominant methods in this light you can start to see strengths and weaknesses.

#### a) Molecular Absorption UV 254nm

Many compounds absorb ultraviolet (UV) or visible (Vis.) light. The diagram below shows a beam of monochromatic radiation of radiant power  $P_0$ , directed at a sample solution. Absorption takes place and the beam of radiation leaving the sample has radiant power  $P$ .



The amount of radiation absorbed may be measured in a number of ways:  
Transmittance,  $T = P / P_0$   
% Transmittance,  $\%T = 100 T$   
Absorbance,  
 $A = \log_{10} P_0 / P$   
 $A = \log_{10} 1 / T$   
 $A = \log_{10} 100 / \%T$   
 $A = 2 - \log_{10} \%T$

Beer-Lambert's Law defines the relationship between absorption and concentration.

$$A = kbc$$

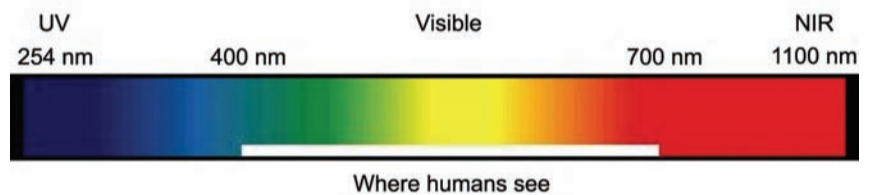
Where;

- A = absorbance
- K = the molar absorptivity
- B = path length
- C = concentration

Adopting the principal of light absorption at a wavelength of 254nm in the UV spectrum as the means of measuring organic compounds in boiler water condensate, assumes that the molar absorptivity of the matrix of the compounds in the sample will remain constant.

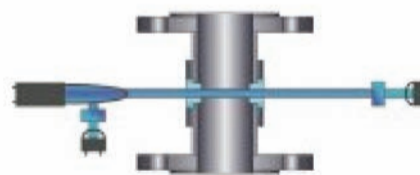
Below is a spectrum showing the position of the required light source with reference to visible light.

A typical measuring cell is shown below:



#### UV - Ultraviolet Light Absorption

Single Channel Light Absorption  
(single detector, with lamp reference detector)



This method offers one major advantage and that is one of simplicity, once a light source, measuring cell and detector have been installed in the condensate stream, the operation and maintenance issues are minor.

However, the reality of the application is far more complex than the installation would indicate. Since the main source of absorption is  $-C=C-$  double bonds and aromatic ring structures that absorb UV light at 254 nm, the assumption as stated above is that the matrix/molecular absorptivity is a constant. In reality the compounds and ratio of the compounds that can be present in the condensate will change, hence the ability to calibrate such a system is difficult.

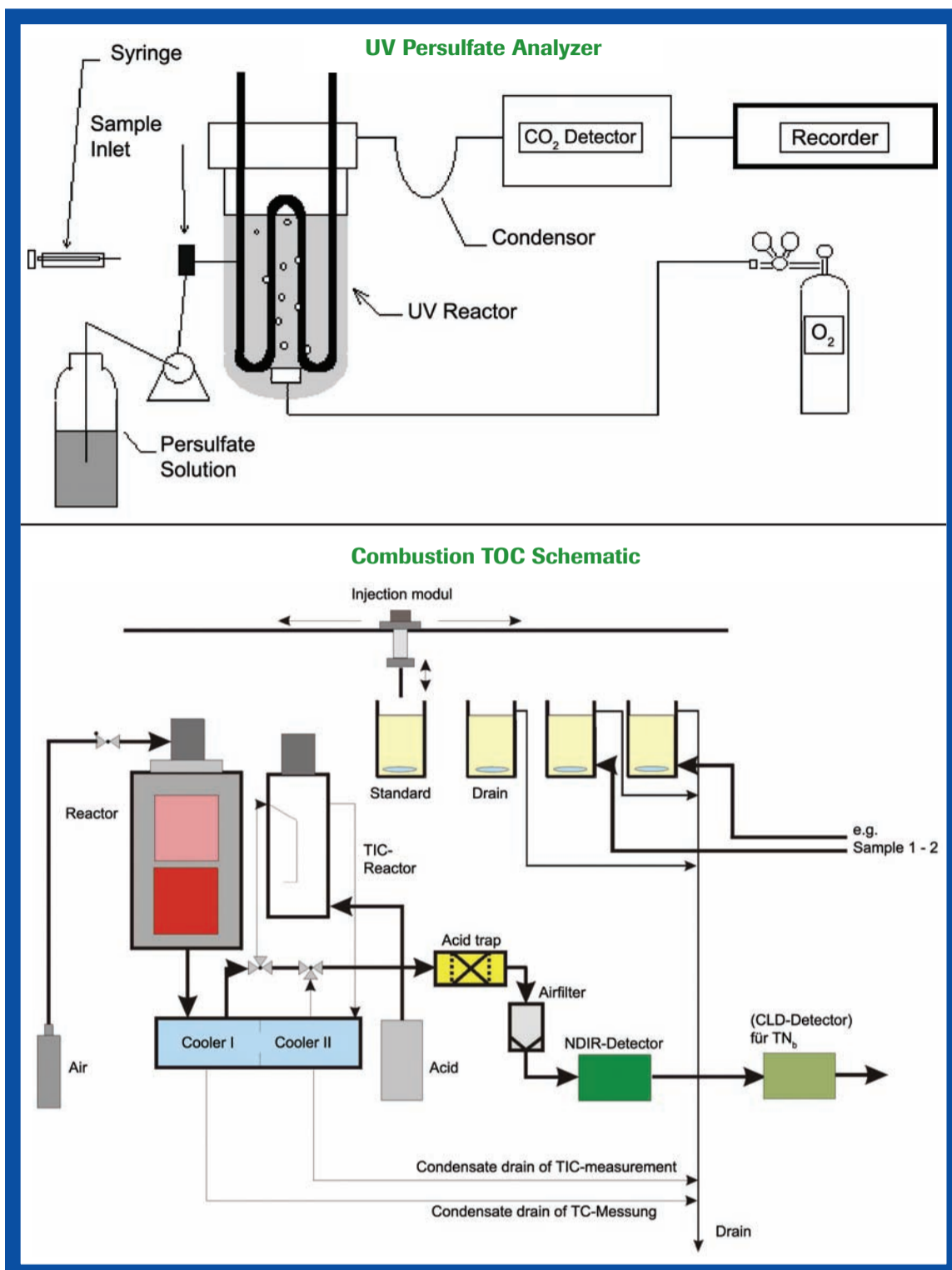
The issue of calibration has to be addressed, with the degree by which an organic compound will or will not absorb at 254nm being a function of double bonds, leading to the limitation of this method. Since organic compounds that do not have double bonds will not absorb, they will be excluded from the measurement, hence the method is compromised. Add to this that organic compounds having different numbers of double bonds will absorb different quantities of UV light, (different values for K in Beer's Law), obtaining a reliable calibration is difficult if not impossible in some cases.

The UV 254nm measurement has its place in the measurement of organic compounds, however the limitations of the method do not make it the first choice for monitoring boiler water condensate.

#### b) UV Persulfate TOC

This method utilizes the combination of acidified persulfate and the energy provided by 254 nm UV light to breakdown and oxidize organic molecules to release carbon dioxide, which is subsequently measured using an infrared detector.

At the top of the following page is a simple schematic of an early UV Persulfate Analyzer.



Over the years there have been advancements made in UV persulfate methods and the analyzers utilizing this methodology. One area that has seen improvement is the advent of more efficient high-energy UV sources. Modern lamps have the ability to produce strong UV emissions at 185 nm and 254 nm, which stimulate the production of hydroxyl (OH.) free radicals in the solution being analyzed. It is these free radicals that assist the oxidation of the organic compounds in the sample.

The persulfate has the advantage of oxidizing the majority of dissolved organic carbon (DOC) and will not have the calibration issues associated with the UV Adsorption method. The UV Persulfate TOC provides a reliable way of detecting organic contaminants in condensate, however there are a number of issues that need to be considered before installing this type of analyzer.

When deciding on the suitability of an analyzer for a condensate application one of the main deciding factors is response time. When organic contamination occurs the faster it is detected the less potential for major upsets. With the persulfate technique the method is one of continuous analysis that would apparently be ideal for this application. However unlike pH & conductivity analysis, which are also continuous, were the results are as close to instantaneous as feasibly possible, the results from a persulfate TOC are not instantaneous. When installing these type analyzers the cycle time for analysis or the retention time has to be considered. The typical retention time, that being the time from when a



sample enters the analyzer and the time that a value is recorded, is 8 min. The plant has to make a decision if the potential harm caused by an upset of 8 min can be tolerated. The remaining considerations relate to the degree of maintenance required, and the cost of ownership. The most obvious maintenance, cost of ownership item is the reagent consumption. The analyzer uses a solution of acidified sodium persulfate and the estimated cost has been quoted in the area of \$5,000.00 per year. Together with the costs associated with preventative maintenance items, a total annual cost is estimated in excess of \$7,000 per year.

With the continuing concerns with cost of ownership and maintenance time added to the analytical restrictions of the method, the use of persulfate TOC analysis for boiler water condensate is also not 100% ideal.

#### d) TOC Analysis using High Temperature Combustion

One of the classic methods of determining TOC is High Temperature combustion. This method utilizes a combustion furnace operating at temperatures of 680 to 1,200 degrees Centigrade. Effectively, high temperature in the presence of oxygen burns all organic compounds contained in the sample to produce carbon dioxide. The resulting carbon dioxide is measured using an infrared detector, (see diagram below).

Combustion TOC analyzers for boiler water condensate applications have a number of advantages depending on the design criteria of the analyzer. The three greatest advantages if the combustion techniques are:

- 1) Complete combustion of all organic compounds in the condensate sample.
- 2) Analysis time

- 3) Little or no reagent consumption.

Complete combustion of all the available organic compounds in a condensate sample insures that all organic contaminants will be detected and corrective action can be taken before serious problems occur. This makes it the most secure method for condensate applications from an analytical perspective.

Modern combustion TOC analyzers use batch analysis as apposed to continuous with a cycle/response time of 1 min., the quickest on the market today.

The second advantage being cost of ownership, with the combustion technique is there are no reagents required and depending on the design of the analyzer there is little preventative maintenance required.

Today's advances in combustion TOC technology have removed many if not all of the disadvantages previously associated with this technique. With combustion systems using temperatures <1,000 degrees Centigrade there is a need for the introduction of a catalyst in the furnace to facilitate complete combustion. This resulted in increased maintenance and cost of ownership. The latest furnace technologies have resulted in combustion temperatures of 1,200 degrees Centigrade. At this temperature the need for a catalyst has been removed. One other limitation of the combustion technique that has been eliminated is the detection limit. The detection limit of combustion systems have been limited by the volume of sample that could be introduced into the furnace. The latest technology enables volumes of up to 4 ml's to be introduced for one analysis. Combine this with state of the art IR CO<sub>2</sub> detectors with a measuring range of 0 - 50 mg/l detection limits of 10 ug/l are obtained.



A system as shown uses combustion temperatures of 1,200 degrees Centigrade, no catalyst, sealed loop sample injection with a maximum volume of 4 ml's, detection limits of 10 ug/l, no reagents, and an annual cost of ownership of <\$1,500.00.

With the need for fast analysis, accurate results, low cost of ownership, and reliability being key factors in the decision making process the following factors need to be considered.

- 1) Analytical reliability of the method. Has the technique the capability to provide detection of all the organic compounds that could be found in the condensate?
- 2) Response Time. Time that it takes to obtain a result on a given sample.
- 3) Calibration. Can the method be calibrated to cover all matrix variations and variables?
- 4) Reagent consumption. What are the reagents required, their consumption, and their costs?
- 5) Cost of Ownership. Together with the reagent consumption and costs, what are the annual consumable item costs, and what is the time required to maintain the analyzer?

If each of these parameters is investigated, a matrix can be developed as seen below:

	Molecular Absorption UV 254nm	UV Persulfate TOC	TOC Analysis using High Temperature Combustion
Analytical Reliability	Poor	Fair	Good
Response Time	Fast	Slow	Fast
Calibration	Poor	Good	Good
Reagent Consumption	None	High	None
Cost of Ownership	Low	High	Low

TOC Analysis using high temperature combustion has the best overall score indicating that it will provide the most satisfactory option for monitoring organic contaminants in boiler water condensate.