REAL TIME ONLINE LIQUID ANALYSIS TO PREVENT PRODUCT LOSS, TO REDUCE ENERGY CONSUMPTION AND TO MINIMIZE WASTE TREATMENT COSTS IN THE CHEMICAL, REFINING AND FOOD INDUSTRIES

Ali Doğan Demir, David Horan, Martin Horan & Seamus O'Mahony
BioTector Analytical Systems Ltd.
Raffeen House, Ringaskiddy,
County Cork, Ireland.
ademir@biotector.com

KEYWORDS

TWO STAGE ADVANCED OXIDATION, TOC ANALYSIS, COD, PRODUCT LOSS

ABSTRACT

Product losses can be prevented and energy and waste treatment costs can be reduced significantly by means of real-time online Total Organic Carbon (TOC) monitoring in a process or waste water stream in the chemical, refining and food industries. TOC, measured by the BioTector Two Stage Advanced Oxidation technology, has been proven to have a direct relationship to the content of the products in a process stream or waste water stream leaving a production facility. This direct relationship is possible because this oxidation method is able to include the organic content of the particulates, fibers and sludge, which are present in the liquid sample, in the TOC measurement, without any filtration or homogenization process. This technology has been specifically developed to operate in very difficult applications and has already become a global solution for reliable TOC analysis in the most demanding chemical and refining industries. The benefits of this technology are now being applied in the food processing industry. The process and waste waters in the food industry is monitored continuously with the objective of determining the presence of any lost products in the streams. Reducing product loss results in significant savings in the raw materials, in the energy consumption and in the water and waste water treatment charges. This objective has been previously attempted by using laboratory and online Chemical Oxygen Demand (COD) measurement; however, these methods have proven to be unreliable and expensive. The unfiltered measurement of TOC has been demonstrated to be more successful than COD measurement in the chemical, refining and food processing industries. This is due to the closer relationship which exists between the TOC and the bulk products, which may be lost in the waste streams. COD measurement may be a useful measurement for determining the biological load to the waste water treatment plant. However, TOC measurement is much more useful when identifying the quantities of products, which could be lost in physical quantities, measured in pounds or kilograms, not in terms of biological loading. In this study, it has been demonstrated that TOC measurement has a strong relation with the bulk product loss in chemical, refining and food processing plants. The product loss can be reduced by up to 20% in dairy plants using TOC analysis. Up to 30% reduction in effluent costs can be achieved. This means more product in production and less product in waste water treatment plant.

INTRODUCTION

Most industries monitor the organic loading of its waste waters by measuring the COD levels before discharging them into public waterways in accordance with the local government regulations. In recent years, with the development of the Two Stage Advanced Oxidation technology (TSAO), it is possible to measure the TOC content of samples, which were not possible with the traditional TOC measuring methods such as thermal combustion and UV persulfate oxidation [1]. This technology has gradually led to a change in the objective of the organic load monitoring in many industries because it is now viable to monitor the TOC content of the process samples and reduce the product loss, which in turn reduces the organic loading in the waste water, resulting in significant savings in production and effluent costs.

The COD analysis, which typically takes two hours in a laboratory, was developed as an alternative to the five-day Biochemical Oxygen Demand (BOD_5) test, due to the direct linear correlation between the COD and BOD measurements. Despite the fact that it can be carried out online or offline, the COD analysis is an ineffective measurement technique for many industries. This analysis is time consuming and inaccurate for the determination of the contamination levels and the organic loading in the waste water. The result is too late for any process decision in a plant or for any modification in the waste water treatment process. Therefore, the requirement for a laboratory offline analysis, the inconsistency of the COD readings in an online instrument, and the high costs of the COD testing make this analysis unattractive in many industries.

Dissolved oxygen, which is needed to break down and oxidize the organic compounds by biological activity, is measured by the BOD method. There is a wide variation in the BOD results because all organic compounds have a different BOD value, as the test is affected by many parameters such as sample pH, temperature, initial dissolved oxygen levels and the ability of the microorganisms to degrade specific organic matter. COD is a similar method to BOD, but chemical oxidation is used to oxidize the organics in a sample. Once again, there is a wide variation in the COD results, because all organic compounds have their specific COD value, and because the test is affected by sample parameters such as particulate organic content and volatiles, which are not oxidized completely, and the capacity of the chemical oxidation method to fully oxidize specific organic compounds.

The COD method is generally defined as the equivalent amount of oxygen required to oxidize organic matter in a sample by a strong chemical oxidant. It is a known phenomenon that COD methods do not recover specific organic compounds, which are difficult to oxidize or are resistant to chemical oxidation. As the definition of the COD method also suggests, there is no direct relation between the COD measurement and the bulk product loss in the industry, because COD measures the equivalent amount of oxygen required to oxidize organic matter, not the organic matter directly. The relation between the COD result and the product loss is always indirect and related to the amount of oxygen required to oxidize the organic matter. Therefore, COD analysis can be assumed to be a good water quality measurement technique or an estimate for the organic loading of waste waters in a laboratory. COD measurement is not a good process control or a product loss monitoring tool.

TOC analysis, on the other hand, is a direct measurement of organic carbon in process and waste waters. The organic carbon compounds are oxidized to carbon dioxide (CO_2) by high energy oxidation techniques and the CO_2 concentration, which is directly proportional with the TOC result, is measured using non-dispersive infrared CO_2 analyzers [2]. The advantages and simplicity of the TOC analysis, and the availability of TOC analyzers for laboratory and online applications, make this analysis a very useful and attractive measurement in the industry. Due to the growing preference of TOC as the measuring parameter for many industry users, many countries have changed their regulations to allow TOC measurement as a valid indicator for COD. The existing problems related to the traditional online TOC analysis have been solved with the development of Two Stage Advanced Oxidation technology, which lead to reliable online TOC analysis. This technology has also lead to the development of an online multi-component analyzer, where the analysis of multiple parameters such as TOC, Total Nitrogen (TN) and Total Phosphorus (TP) is now possible in a single analyzer unit, which uses a common oxidation process for the measurement of each parameter [3, 4]. Because of this, the use of TOC TN and TP as parameters for measuring product loss and organic loading of waste water has become increasingly popular in many applications worldwide. Furthermore, the effective correlation, which exists between the TOC and COD results, has now been improved with the additional TN and TP measurements for a particular type of process and waste water samples.

A representative sampling process is critical for the validity of the measurements and for any correlation, which is being established between various analysis methods such as COD and TOC. Samples are generally homogenized as standard before carrying out any type of laboratory analysis. The homogenization process helps include the organics or any target compounds coming from salts, particulates, fibers and sludge etc., which may be present in the liquid sample. It has been recorded that, when samples are filtered using certain pore size filters, the TOC measurement results can be reduced by up to an average of 50% [1]. When samples are taken directly without any homogenization in the laboratory measurement, the analysis results can be significantly lower due to the use of micro-syringes and pipettes, which also act as a certain pore size filter. In online TOC analyzers utilizing the Two Stage Advanced Oxidation technology, 3.2mm internal diameter (ID) perfluoro alkoxy (PFA) tubing is used throughout the sampling and sample injection process. This allows the system to be able to analyze soft particulates up to 2mm outside diameter (OD). It is possible to use such large ID sample tubing and inject large volume of sample into the reaction chamber for the analysis, because the oxidation process utilizes hydroxyl radicals, which are very aggressive oxidizing agents, capable of oxidizing difficult-to-oxidize compounds and samples containing high levels of salts, particulates, fibers and sludge [5]. The use of large ID sample tubing and the injection of large volume sample into the reaction chamber allow the sampling to be more representative and to be carried out without any filtration or homogenization process. This gives the online analyzer system the ability to have a direct relationship with the measured content of the products in a process or waste stream, and also to have a direct correlation with the results of laboratory methods, where sample homogenization is applied.

When online Two Stage Advanced Oxidation TOC or TOC/TN/TP analyzer systems are installed and used to effectively monitor and prevent product loss and to reduce organic loading to the waste water treatment plant, depending on the application and the savings achieved, the cost of the investment is paid within months and in some cases within less than a month. The reduction in product loss and organic loading make the return of investment very successful. In the event of a critical process fault, which can lead to large product losses, or a spill and leak, which can lead to high organic loading to the waste water treatment plant, the online real time monitoring of TOC or TOC/TN/TP with TSAO technology will help detect the problem and result in significant amount of savings in product loss and organic loading. One of the major advantages of the online analysis is the fast cycle time and response, which is typically six minutes for TOC [6], and ten minutes for TOC/TN/TP analysis [7]. The online TOC/TN/TP analysis results are consistent and precise with typically 3% relative standard deviation (RSD). The fast, accurate, and representative online data obtained from the analyzer, help the users to better understand their process, to identify potential and specific problems in their plant and solve them in real time as they occur, and finally to control the relevant processes and improve the plant performance.

In this study, the direct relationship between the product loss and TOC is investigated with examples from the chemical, refining and food industries. The impact of sample filtration and homogenization on the analysis results is demonstrated. The relationship between the TOC result and the product loss is proven with theoretical TOC and COD analysis carried out on real industrial samples and sample constituents. The reduction in production costs by reducing overall lost product, the reduction in energy costs at the point of production by maximizing the recovered product and the reduction in waste treatment cost by reducing the organic loading, which are achievable by means of TOC analysis, are illustrated.

MATERIALS AND METHODS

The efficiency of Two Stage Advanced Oxidation process for the TOC analysis of unfiltered samples is evaluated and proven by analyzing the TOC content of various industrial samples. The effect of sample homogenization and filtering on the TOC results is evaluated by analyzing sample “A” received from an oil refinery in the United States (US) and sample “B” received from a chemical plant in Slovakia. Each specific sample is mixed and split into two flasks. One of the flasks is analyzed by placing the TSAO analyzer’s 3.2mm ID PFA tubing somewhere at the center point of the flask, while the sample is mixed with a magnetic stirrer aggressively. This sample represents the homogenized sample, where all particulate organic and suspended solid matter is included in the TOC result. The other sample is left to settle for a few hours on the bench. The analysis of this sample is carried out without the use of any stirrer. The sample is taken mostly from the top section of the flask, which does not contain any particulate matter. This sample represents the settled sample, where the particulate matter is excluded in the TOC result. The difference in the TOC results obtained from the stirred and settled samples are compared for both types of samples.

The correlation between the online TOC and laboratory COD results has been evaluated analyzing sample “A” received from the oil refinery in the US, sample “C” from a multinational chemical plant in Belgium and sample “D” from a dairy plant in Germany. A Two Stage Advanced Oxidation TOC analyzer is used for the TOC the analysis. A minimum of eight TOC analyses are performed on each sample. The COD contents of the samples are measured with the laboratory HACH DR 5000 Spectrophotometer using the Reactor Digestion COD Method 8000 [8]. In addition, the long term TOC and COD correlation data is obtained from a dairy plant in the Republic of Ireland for sample “E”. An online Two Stage Advanced Oxidation TOC analyzer is used at this site, where the COD analysis is carried out in the plant’s laboratory. The linearity between the long term TOC and COD analysis data is illustrated in subsequent tables and figures.

A theoretical TOC and COD analysis study is carried out on the major sample constituents representing the chemical, refining and food industries. The typical specific major sample constituents of the oil refinery crude oil sample, the chemical plant sample, and the dairy plant sample, representing sample “A”, “C” and “E” respectively are obtained from the operators in each plant. The theoretical TOC and the theoretical laboratory COD values of all specific constituents of these samples are determined. A basic statistical analysis is carried out and the data is analyzed looking at the coefficient of variation (c_v) values, which are the inverse of the signal to noise ratio, for both TOC and COD values of these samples. The objective of the analysis is to determine the statistically most stable response, which would have the direct and better relationship to the content of the products in a process or a waste water stream.

The reduction in product loss and the consequent reduction in organic loading to waste water treatment plant, achieved with the use of Two Stage Advanced Oxidation TOC analyzer, are illustrated with example figures from the dairy industry. Table I below summarizes the samples, the industry they represent and the countries the samples are received from.

TABLE I - SAMPLE, REPRESENTED INDUSTRY AND COUNTRY INFORMATION

Sample	Industry	Country
A	Oil Refinery	United States
B	Chemical	Slovakia
C	Chemical	Belgium
D	Dairy	Germany
E	Dairy	Ireland

RESULTS AND DISCUSSIONS

Figure 1 illustrates the importance of representative sampling with the TOC results obtained from the stirred and settled oil refinery sample "A" as measured with the Two Stage Advanced Oxidation TOC analyzer.

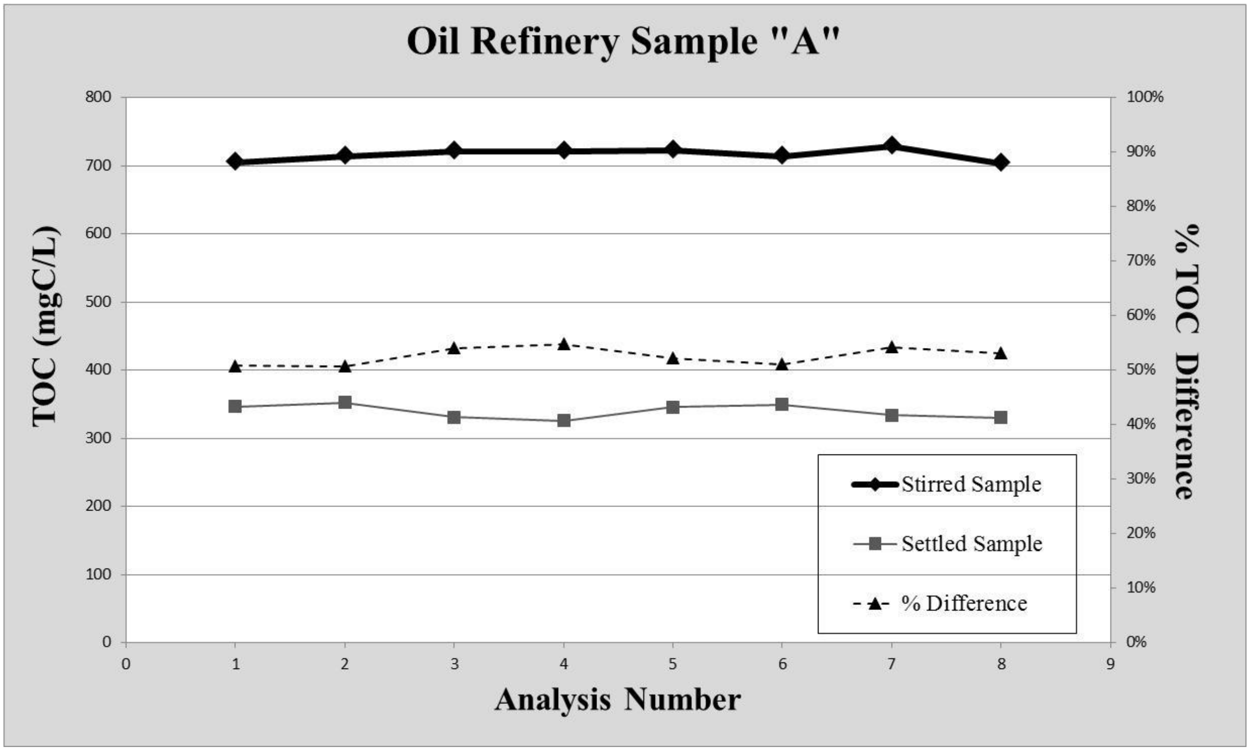

FIG. 1 - EFFECT OF REPRESENTATIVE SAMPLING ON THE TOC READINGS IN OIL REFINERY SAMPLE

As can be seen from Figure 1, the mixing process and the sampling of particulate and suspended matter during the Two Stage Advanced Oxidation TOC analysis have a significant effect on the TOC readings of the oil refinery sample. The TOC results have dropped by an average of 52% between the stirred and settled samples. When this sample is filtered or when the sampling is carried out using micro-syringes as in the thermal combustion analyzer systems, a greater impact can be expected. It is worth noting that, it is possible to see such an impact with the use of Two Stage Advanced Oxidation process, where the particulate and suspended organic matter is sampled and recovered during the TOC analysis. With the use of traditional online or laboratory analyzers, such as the thermal combustion analyzers, it may not have been possible to see such impact because the sampling of in these system are carried out using very small ID sample tubing (e.g. 0.8mm), and therefore the sample would be screened during the sampling process and the particulate organic content of the sample would be excluded from the TOC result.

Figure 2 shows the impact of stirred and settled sampling on the TOC results as obtained from the chemical plant sample "B".

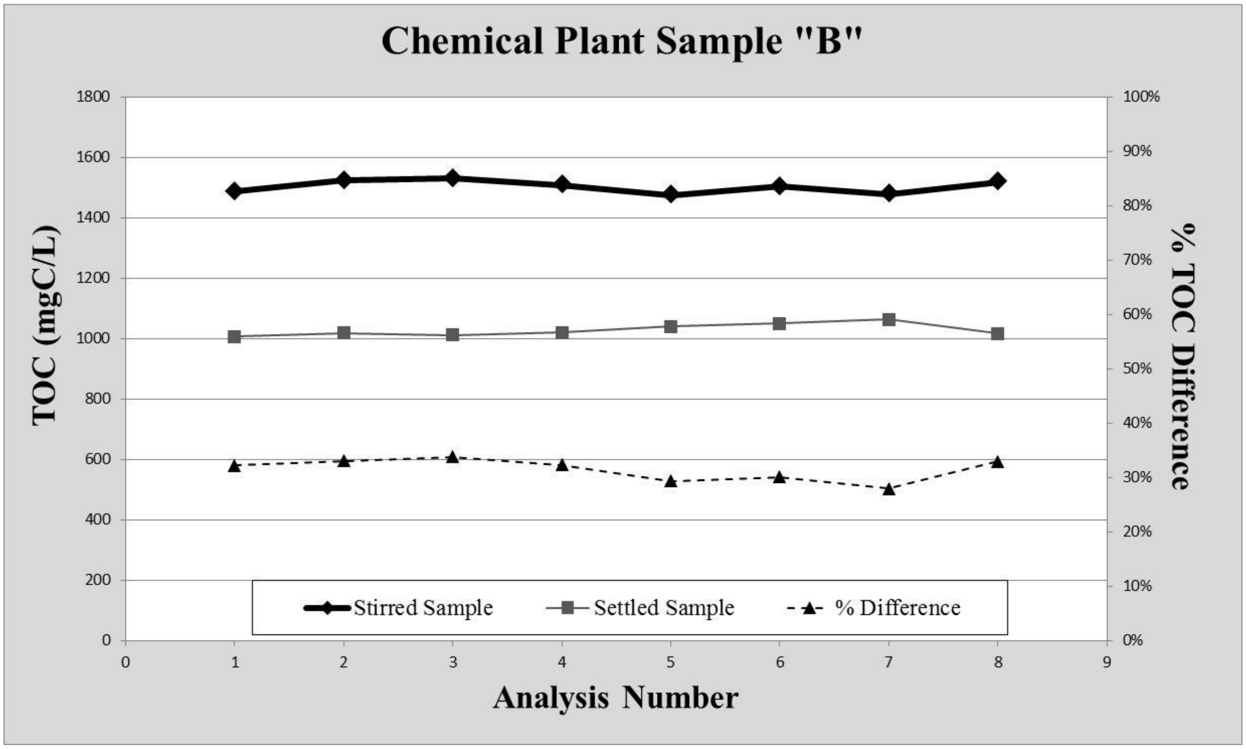

FIG. 2 - EFFECT OF REPRESENTATIVE SAMPLING ON THE TOC READINGS IN CHEMICAL PLANT SAMPLE

Figure 2 also shows that the mixing process and the ability of the Two Stage Advanced Oxidation TOC analyzer to measure a representative sample without any need for a filtration or screening process, significantly changes the results and supplies the user more accurate and representative analysis data. This helps the user to better control their process and make relevant correct decisions in the event of a process problem or spill on site. In some applications, it is possible that the particulate and suspended organic materials are excluded from the TOC result intentionally using a filtering system or a certain size filter or screen mesh. It is also possible that these organics are excluded unintentionally using micro-syringes and pipettes during the sampling process. Regardless of these facts, the objective of the TOC analysis is always to identify specific process problems, to reduce product loss and to reduce organic loading to the waste water treatment plant. In order to achieve these objectives, representative sampling and accurate analysis of the sample, which includes all particulate and suspended organic matter in the TOC result, would be essential. As demonstrated above, Two Stage Advanced Oxidation TOC analyzer system has proven to be able to achieve these objectives with ease.

Table II below shows the correlation between the online TOC results and the laboratory COD measurements as obtained from the oil refinery sample "A", the chemical plant sample "C" and the dairy plant sample "D".

TABLE II - ONLINE TOC and LABORATORY COD CORRELATION FOR OIL REFINERY, CHEMICAL AND DAIRY PLANT SAMPLES

Sample Name and Industry	Online TSAO TOC (mgC/L)	Laboratory COD (mgO/L)	COD/TOC Ratio (COD Factor)
A (Oil Refinery)	3909.6	16100	4.1
C (Chemical Plant)	10851.0	39200	3.6
D (Dairy Plant)	3010.1	7740	2.6

The TOC results tabulated in Table II are the average of eight TOC analyses, obtained from the Two Stage Advance Oxidation TOC analyzer. The repeatability of the TOC readings is better than ±3% for all samples. As can be seen in the table, there is variation in the COD/TOC ratios, which are generally referred as “COD factors”, between each specific industry. This is due to the fact that each sample is composed of different types of organics, which contains various amounts of carbon and oxygen atoms in their molecular structure. This creates a variation in the COD factors between samples of specific industries. This variation may also be present between the specific process samples in the same industry. The COD factors typically vary from 2 to 4 for the majority of the cases. However, there are applications which may require considerably higher or lower factors, depending on the specific sample constituents. Figure 3 shows the online TOC and laboratory COD correlation for sample “E” as obtained from a dairy plant in Ireland.

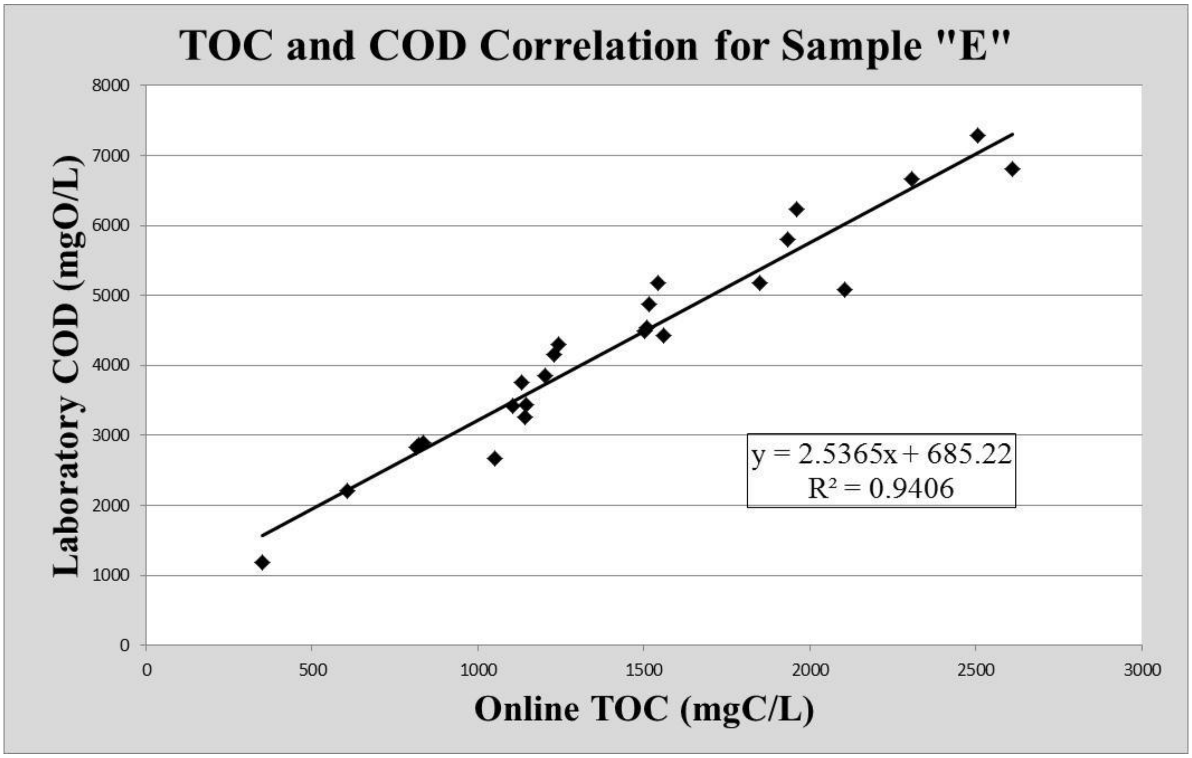

FIG. 3 - DAIRY PLANT TOC AND COD CORRELATION GRAPH

As can be seen in Figure 3, there is a linear relationship between the online TOC and laboratory COD measurements. The average COD factor used in this dairy plant is 3.1 with an RSD of 10%. It should be noted that the relatively high relative standard deviation in the COD factors is due to the variation in the laboratory COD analysis as discussed above. The direct relationship between TOC and COD always exists in all types of applications in industry. However the coefficient of determination values (R^2), obtained from the linear regression between laboratory COD and online Two Stage Advanced Oxidation TOC, are always better in dairy plants in general and also in this specific dairy plant with an R^2 value of "0.9406". This is due to the fact that Two Stage Advanced Oxidation process is able to include the fats, the particulate and suspended organic materials in the TOC result. Therefore a better correlation is achieved with the laboratory COD analysis carried out on homogenized samples.

Table III below shows the selected constituents of an oil refinery crude oil sample, the % average weight/weight (w/w) contribution of each sample constituent, the theoretical expected TOC and COD values with the COD factors and the corresponding coefficients of variation for TOC and COD as obtained from the average and the standard deviation values. As crude oil contains a very wide variety of compounds, including liquid, gas and solid hydrocarbons, and because there is a wide variation in the % composition, the selected constituents tabulated below form 23.1% of the petroleum products.

TABLE III - THE COMPOSITION AND THE CORRESPONDING THEORETICAL TOC AND COD VALUES OF AN OIL REFINERY CRUDE OIL SAMPLE

Compound	Chemical Formula	% w/w Contribution	Theoretical TOC (mgC/L)	Theoretical COD (mgO/L)	COD Factor
n-Hexane	C_6H_{14}	1.25	10454	44088	4.2
n-Heptane	C_7H_{16}	1.55	13006	54452	4.2
n-Octane	C_8H_{18}	1.40	11777	49028	4.2
n-Nonane	C_9H_{20}	1.25	10535	43663	4.1
n-Decane	$C_{10}H_{22}$	1.80	15194	62748	4.1
n-Undecane	$C_{11}H_{24}$	1.70	14368	59160	4.1
n-Dodecane	$C_{12}H_{26}$	1.70	14384	59075	4.1
Dimethylbutane	C_6H_{14}	0.09	753	3174	4.2
Methylpentane	C_6H_{14}	0.70	5854	24689	4.2
Ethylpentane	C_7H_{16}	0.05	420	1757	4.2
Dimethylpentane	C_7H_{16}	0.40	3356	14052	4.2
Trimethylpentane	C_8H_{18}	0.02	168	700	4.2
Methylethylpentane	C_8H_{18}	0.04	336	1401	4.2
Methylhexane	C_7H_{16}	1.05	8811	36887	4.2
Dimethylhexane	C_8H_{18}	0.32	2692	11206	4.2
Dimethylheptane	C_9H_{20}	0.20	1686	6986	4.1
Methyloctane	C_9H_{20}	0.75	6321	26198	4.1
Cyclopentane	C_5H_{10}	0.05	428	1711	4.0

Methylcyclopentane	C_6H_{12}	0.60	5138	20532	4.0
Dimethylcyclopentane	C_7H_{14}	1.16	9933	39695	4.0
Trimethylcyclopentane	C_8H_{16}	0.91	7792	31140	4.0
Dimethylcyclohexane	C_8H_{16}	0.30	2569	10266	4.0
Ethylcyclohexane	C_8H_{16}	0.20	1713	6844	4.0
Cyclohexane	C_6H_{12}	0.70	5994	23954	4.0
Trimethylcyclohexane	C_9H_{18}	0.20	1713	6844	4.0
Benzene	C_6H_6	0.22	2030	6758	3.3
Toluene	C_7H_8	1.30	11863	40638	3.4
Ethylbenzene	C_8H_{10}	0.20	1810	6330	3.5
Xylene	C_8H_{10}	1.78	16111	56337	3.5
Methylethylbenzene	C_9H_{12}	0.35	3148	11183	3.6
Trimethylbenzene	C_9H_{12}	0.63	5666	20129	3.6
Tetramethylbenzene	$C_{10}H_{14}$	0.2	1790	6438	3.6
Biphenyl	$C_{12}H_{10}$	0.02	187	602	3.2
Average	-	-	6000	23899	4.0*
Standard Deviation	-	-	5141	20591	-
Coefficient of Variation (c_v)	-	-	0.8568	0.8616	-

* weighted average

Because of the differences in the % w/w contribution of each compound present in the crude oil sample, and the fact that the COD factors of high concentration compounds will contribute more than the others, the weighted average COD factor is determined.

As can be seen in Table III, the weighted average COD factor “4.0”, obtained from the theoretical TOC and COD analysis, is in very good agreement with the experimental ratio “4.1” found from the online TOC and laboratory COD analysis of oil refinery sample “A” tabulated in Table II above. It should be noted that the % w/w contribution values of each compound listed above are the average values and these values may not represent the actual contribution in a specific sample. For instance, the concentration of n-Heptane can vary from 0.8% to 2.3% and the concentration of n-Nonane can vary from 0.6% to 1.9% etc. in crude oil. Due to the good correlation between the TOC and COD analysis, any change in the concentration of specific compound would not have a significant impact on the overall result. Therefore, any decision made looking at the TOC results will be valid for the prevention of product loss and thus for the reduction the organic loading in the waste waters.

Even though the coefficient of variation values for the theoretical TOC and COD values are marginally different, there is evidence that the TOC results are less variant and therefore more stable compared to the COD results. This indicates that TOC results will have a better relationship with the content of the products and the overall product loss into the waste water streams in the event of a leak or a spill problem in the oil refinery plant.

Table IV demonstrates the typical constituents of the chemical plant sample “C”, the % average w/w contribution of each sample constituents, the theoretical expected TOC and COD values with the COD factors and the corresponding coefficients of variation for TOC and COD as obtained from the average and the standard deviation values.

TABLE IV - THE COMPOSITION AND THE CORRESPONDING THEORETICAL TOC AND COD VALUES OF CHEMICAL PLANT SAMPLE “C”

Compound	**Chemical Formula**	**% w/w**	**Theoretical TOC (mgC/L)**	**Theoretical COD (mgO/L)**	**COD Factor**
Dimethyldioxolane	$C_5H_{10}O_2$	0.0021	12	43	3.5
Morpholinopropane sulfonicacid	$C_7H_{15}NO_4S$	0.016	64	287	4.5
Hydroxyacetone	$C_3H_6O_2$	0.089	433	1346	3.1
Dipropyleneglycol methylether	$C_7H_{16}O_3$	2.33	13218	47793	3.6
Monopropyleneglycol	$C_3H_8O_2$	0.18	852	3028	3.6
Methylvaleraldehyde	$C_6H_{12}O$	0.0157	113	426	3.8
Tripropyleneglycol methylether	$C_{10}H_{22}O_4$	0.37	2155	7748	3.6
Average	-	-	2407	8667	3.6*
Standard Deviation	-	-	4826	17462	-
Coefficient of Variation (c_v)	-	-	2.0052	2.0147	-

* weighted average

Due to the differences in the % w/w contribution of each compound present in the chemical plant sample “C”, the weighted average COD factor is determined. As can be seen in Table IV, the weighted average COD factor “3.6”, obtained from the theoretical TOC and COD values, is in excellent agreement with the experimental COD factor “3.6” measured from the TOC and COD analysis of sample “C” tabulated in Table II above. As in the crude oil example above, it should be noted that the % w/w contribution values of each compound listed for the chemical sample “C” above are the average values and these values may not represent the actual contribution in a specific sample. For example, the concentrations of dipropyleneglycolmethylether and tripropyleneglycolmethylether can drop significantly in this specific sample. However, due to the established correlation between the TOC and COD, any process decision made and any organic loading to waste waters decision made looking at the TOC results will be accurate. The fact that TOC analysis is a much faster response, which is typically available within six minutes, the early detection of a process problem and the early decision for the reduction of the organic loading to the waste water treatment plant are extremely beneficial for the plant operators.

As can be seen from the coefficient of variation values for the theoretical TOC and COD values in Table IV above, once more, there is evidence that the TOC results are less variant and more stable than the COD results. This shows that TOC results have a better correlation with the product contents and in the event of a spill or leak, with the lost product into the waste water streams in the chemical plants.

Table V illustrates the typical constituents of the dairy plant sample “E”, the % average w/w contribution of each sample constituents, the theoretical expected TOC and COD values with the COD factors and the corresponding coefficients of variation for TOC and COD as obtained from the average and the standard deviation values. As the milk composition varies depending on the animal species and the breed it is obtained from, as well as the animal's feed, the gross composition tabulated below is assumed to be for cow milk, containing ~5% lactose, ~3.5% fats, ~3% proteins, ~0.5% minerals/ash and the balance water. Milk fat is assumed to be triglyceride, which forms ~98% w/w of the total milk fat. Because there are approximately twenty two different types of amino acids that can combine and form protein chains, nine essential amino acids are selected and analyzed assuming similar percent contribution from each of the twenty two amino acids.

TABLE V - THE COMPOSITION AND THE CORRESPONDING THEORETICAL TOC AND COD VALUES OF DAIRY PLANT SAMPLE “E”

Compound	**Chemical Formula**	**% w/w**	**Theoretical TOC (mgC/L)**	**Theoretical COD (mgO/L)**	**COD Factor**
Lactose	$C_{12}H_{22}O_{11}$	5.0	21055	56090	2.7
Triglyceride	$C_{42}H_{77}O_6$	3.5	26058	96212	3.7
Histidine	$C_6H_9N_3O_2$	0.14	650	3393	5.2
Isoleucine	$C_6H_{13}NO_2$	0.14	769	3330	4.3
Leucine	$C_6H_{13}NO_2$	0.14	769	3330	4.3
Lysine	$C_6H_{14}N_2O_2$	0.14	690	3524	5.1
Methionine	$C_5H_{11}NO_2S$	0.14	564	2927	5.2
Phenylalanine	$C_9H_{11}NO_2$	0.14	916	3322	3.6
Threonine	$C_4H_9NO_3$	0.14	565	2350	4.2
Tryptophan	$C_{11}H_{12}N_2O_2$	0.14	906	3510	3.9
Valine	$C_5H_{11}NO_2$	0.14	718	3155	4.4
Average	-	-	4878	16467	3.3*
Standard Deviation	-	-	9303	30844	-
Coefficient of Variation (c_v)	-	-	1.9071	1.8730	-

* weighted average

The weighted average COD factor is determined as 3.3 taking the differences in the % w/w contribution of each compound present in the dairy plant sample “E”.

As can be seen from the coefficient of variation values for the theoretical TOC and COD values in Table V above, unlike the oil refinery and chemical plant samples, the theoretical TOC values of dairy plant sample are slightly more variant than the COD results. This is because of the composition of milk, which mainly consists of sugars, fats and proteins. These compounds have a slightly more variation in their carbon content, which varies from 40% to 77%. For instance the carbon concentration in lactose sugar is 41.1%, whereas triglyceride typically contains 75% carbon. The slightly higher variation in TOC results does not mean that the correlation between the COD will be affected. This variation is not a disadvantage either, because the direct correlation between the TOC and the COD always exists.

As can be seen in Table V, the weighted average COD factor “3.3”, obtained from the theoretical TOC and COD values, is in good agreement with the experimental COD factor “3.1”, measured from the long term online TOC and laboratory COD analysis of sample “E” shown in Figure 3 above. Due to the correlation between the TOC and COD analysis, and the fast response of TOC analysis, all process decisions in this plant are based on TSAO TOC analysis results. The adjustment of organic loading to waste water treatment plant is also based on the TOC analysis.

It is estimated that approximately 1.9% of the volume of the processed milk, which forms approximately 90% of this dairy plant’s total waste water load, is lost into drains mostly during the high temperature short time pasteurization process. Assuming an average TOC value of 500mgC/L with a waste water flow rate of 1100 cubic meters per day, this corresponds to approximately $850000 worth lost milk product per year. It has been reported that the product loss has been reduced by up to 20% in this plant by monitoring TOC using the TSAO technology. In specific incidents, product loss reduction greater than 37% has been achieved. By means of controlling plant operation using TSAO TOC analysis, the water consumption, which varies typically from four to ten liters per kilogram of milk, depending on the specific process in the dairy plant, has been successfully reduced to as low as one liter per kilogram of milk. In parallel with the reduced water consumption and reduction in the product loss, up to 30% reduction in effluent costs is achieved. Reduction in water consumption has decreased water and waste water charges and generated revenue for the plant. The cost of additional in plant water treatment and the energy consumption to heat water have also been reduced significantly.

CONCLUSIONS

In this study, it is proven that there is a direct relationship between the product loss and TOC analysis by Two Stage Advanced Oxidation process, with examples from the chemical, refining and food industries. The importance of sample filtration and homogenization on the analysis results and the ability of Two Stage Advanced Oxidation process to include particulate and suspended matter in online TOC result without any filtration process are demonstrated with real time sample analysis examples. The relationship between TOC and the product loss is proven by the Two Stage Advanced Oxidation TOC analysis, which has a direct and more stable correlation with the contents of the products in chemical, refining and dairy industry.

An increased organic loading to waste water means wasted products and lost revenue. With the use of TOC analysis by means of Two Stage Advanced Oxidation, it is demonstrated that the motoring of the TOC content of the process samples in the chemical, refining and dairy industry and the reduction of product loss, which in turn reduces the organic loading in the waste waters, resulting in significant savings in production and effluent costs, are possible.

The benefits of TOC analysis achieved in a dairy plant is shown with real life examples in the reduced product losses and thus reduced organic loading to waste waters, reduced water usage, reduced waste water charges and reduced energy consumption.

TOC analysis by Two Stage Advanced Oxidation provides;

- reduction in product losses and increase in production efficiency
- reduction in organic loading to waste waters by minimizing waste
- cut back in water consumption
- significant savings in production costs
- substantial savings in effluent costs
- considerable savings in energy consumption
- operators data to understand specific process problems and to achieve higher plant performance
- prevention of negative environmental impacts

REFERENCES

1. Demir, A.D., Horan, M. and O'Mahony, S., "Two-Stage Advanced Oxidation Process as an Alternative to the Thermal and UV-Persulfate Oxidation for TOC Analysis", S08-1-P017-Horan, The Instrumentation, Systems and Automation Society, 51st Analysis Division Symposium, April, 2006, Anaheim, CA.

2. Eaton, A.D., Clesceri, L.S., Rice, E.W. and Greenberg, A.E., "5310 Total Organic Carbon (TOC), A, B, C & D.", Standard Methods for the Examination of Water & Wastewater, 21st Centennial Ed., American Public Health Association (APHA), American Water Works Association (AWWA), Water Environment Federation (WEF), Washington, D.C., 2005, pp. 4-130.

3. Horan, M., Demir, A.D., O'Mahony, S., Horan, D., Brennan, E. and Ruzicka, D., "Development of BioTector Multi-Component Analyzer for TOC, TN and TP Analysis Incorporated with Two-Stage Advanced Oxidation Process", The Instrumentation, Systems and Automation Society, ISA Calgary 2007 Show & Conference, April 11 & 12, 2007, Stampede Park, Calgary, Alberta, Canada.

4. Horan, M., Demir, A.D., O'Mahony, S. and Horan, D., "A Discussion on the Significance of Complete Oxidation of all Oxidizable Compounds Present in a Liquid Sample, where a Target Component to be Analyzed Requires Oxidation Prior to Measurement", 027-Demir, The Instrumentation, Systems and Automation Society, The 54th Annual Symposium of the Analysis Division, "Analytical Solutions for Energy Optimization & Environmental Compliance", April, 2009, Houston, TX.

5. Horan, M., Demir, A.D., O'Mahony, S. and Horan, D., "Online TOC Analysis by Two Stage Advanced Oxidation Process for Applications Containing High Levels of Salts", 004-Demir, The Instrumentation, Systems and Automation Society, The 55th Analysis Division Symposium, "Analytical Solutions in a Not So 'Big Easy' Economic Environment", April, 2010, New Orleans, LA.

6. O'Mahony, S., Horan, M. and Demir, A.D., "Two-Stage Advanced Oxidation Chemistry", Confidential Internal Report CIR 0003, BioTector Analytical Systems Ltd., Co. Cork, Ireland, September, 2002.

7. Demir, Ali Doğan, "Analysis of Total Phosphorus with Two-Stage Advanced Oxidation Process", Confidential Internal Report 17, BioTector Analytical Systems Ltd., Co. Cork, Ireland, October, 2003.

8. "Chemical Oxygen Demand", Water Analysis Handbook, 4th Edition, HACH Company, Colorado, 2002, pp. 743-750.