

Application Note

By: Stephen Lawson

Abstract

Building on nearly 40 years of design and manufacturing experience, Teledyne Tekmar introduces its fifth generation Total Organic Carbon (TOC) UV/Persulfate analyzer, The Fusion. The Fusion offers increased flexibility, software intelligence and user-friendliness making this analyzer ideally suited for demanding laboratory needs. By implementing the patent-pending Static Pressure Concentration (SPC) technology, the Fusion is able to achieve unprecedented low-end sensitivity from a Non-Dispersive Infrared (NDIR) detector. The Fusion demonstrates excellent precision at low ppb (parts per billion) levels, along with the ability to minimize carryover.



KEY WORDS:

Fusion, Total Organic Carbon (TOC), Total Carbon (TC), Inorganic Carbon (IC), TOC analyzers, Non-Dispersive Infrared Detection (NDIR), pharmaceutical, drinking water, waste water

Introduction

Total Organic Carbon (TOC) in water is an important analytical parameter in evaluating water quality. Measurement of the TOC concentration plays a critical role in a variety of industrial and environmental applications. The Fusion and TOC TekLink™ Software combine to provide a wide range of user-friendly features and reliable data analysis. The TOC TekLink™ software provides the user with unattended auto-calibration scheduling, automatic dilution capabilities using stock standards or samples, universal calibration and blank methods for all detector ranges. Automated self-diagnostic tools, 21 CFR functionality - Electronic Records and Electronic Signatures (ERES), exportable reports in various formats, and simple sample scheduling with minimal method development are also new features standard with the Fusion. Default analytical parameters are set for Total Carbon (TC), Total Organic Carbon (TOC), Inorganic Carbon (IC) and Total Organic Carbon by difference (TC-IC) analyses. The range of detection is from 0.2 µg C/L - 4,000 mg C/L with carryover of less than one percent.

Hardware

Instrument Hallmarks

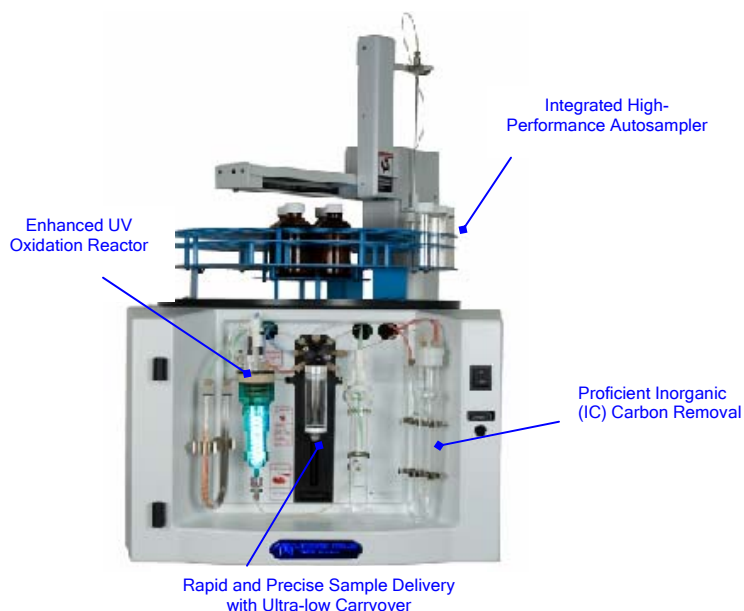


Figure 1 Hallmarks of the TOC Fusion

The Fusion is divided into four main compartments – an integrated autosampler and needle housing; a visible wet chemistry section where all sample manipulations occur; the Mass Flow Controller (MFC), the valves needed to route gas flow, an internal water removal system – Permeation Dryer, and the NDIR detector and the electronics needed to control the instrument. Grouping like compartments allows for easier maintenance as well as separation of the electronics and valves preventing components from possible liquid exposure, which could cause damage, in the unlikely event of valve failure.

There are three autosampler tray sizes:

- * 75 position; 40mL vials
- * 90 position; 55mL test tubes
- * 120 position; 20mL test tubes

All tray sizes have four 125ml bottle positions in the center of the rack.

Directly below the autosampler, a uniquely designed and improved automated syringe delivery system allows for remarkable precision and accuracy. The Fusion handles all liquid movement through a redesigned seven-port valve that is capable of accurately delivering 0.5-25 mL volumes in 20 μ L increments.

A dedicated IC chamber prepares samples for TOC analysis by adding phosphoric acid to the untreated sample and sparging away inorganic carbon. Between the Syringe Pumper and the IC chamber is a highly efficient mist trap for removing moisture from the sample gas before it enters the NDIR Detector, protecting the detector as well as eliminating possible water interference from the sample.

Sodium Persulfate is added to an enhanced UV reactor, located left of the Syringe Pumper, oxidizing all of the carbon to CO₂ with the aid of an ultraviolet light. This newly designed UV Reactor increases sample conservation and delivers better UV radiation interaction between samples and the oxidant. The Fusion utilizes an enhanced halogen scrubber that removes chloride contained within the sample gas as it passes through on its way to the NDIR detector.

Seven valves direct the gas flow controlled by the MFC. The combination of valves and the MFC allows for mode-to-mode changes to the flow rate, and the user to optimize the sparge flow of the sample, resulting in lower gas usage since flow rates can be set instantly. Higher flow rates sweep the flow path between samples decreasing the time of analysis. Along with CO₂ gas, an inert carrier gas from the UV oxidation chamber carries water vapor through the mist trap to the improved permeation dryer. The permeation dryer has a smaller internal diameter that permits more surface area exposure to the carrier gas stream, which improves its capacity to remove water vapor

Inside the right partition of the Fusion is the detector designed to tolerate higher concentrations of SO₂/SO₃, moisture and halogens. This newly designed detector uses Static Pressure Concentration (SPC) combined with NDIR technology to achieve unrivaled performance at lower concentrations. With traditional flow through cell detectors like the Phoenix 8000, UV/Persulfate oxidation liberates carbon to create CO₂ gas. The detector measures the adsorption of the infrared light over time as the CO₂ passes through (figure 2). The resulting measurement correlates to a peak. Integration of the peak height correlates to the concentration of carbon in the sample.

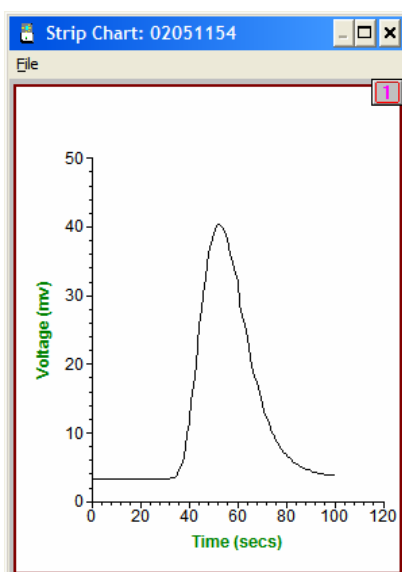


Figure 2 Typical flow-through cell detector gas peak

Anatomy of a flow through cell NDIR detector:

Inside the detector are two detector cells, one front and one rear. Infrared energy traverses through the sample chamber then on to both detector cells. A rotating chopper blade interrupts the infrared energy beam at regular intervals causing changes in the energy levels reaching the detector cell. The pulsing of the infrared energy results a pulsed pressure flow through a mass flow sensor between the detector cells. The mass flow sensor emits an electrical signal proportional to the magnitude of the flow. When there is no carbon dioxide in the sample cell, the maximum amount of infrared energy enters the detector cell. Carbon dioxide displays a unique absorption spectrum when infrared energy passes through it, which allows the NDIR detector to distinguish it from other gases (see figure 5). As the sample cell receives the carbon dioxide gas, it absorbs some of the infrared energy normally sent to the front detector. The reduction of energy entering the forward detector cell causes a decline in its pressure. This results in a flow change between the front and rear detector cells. As the mass flow sensor, located between the front and rear detectors, emits an electrical signal, proportional to the magnitude of the flow between the detectors, there is a corresponding peak displayed usually in millivolts (mV) on the instrument. Once carrier gas purges out carbon dioxide in the sample cell, the detector output signal decreases to its previous level because the flow between the detectors has returned to equilibrium. The mV-seconds area of this peak is the raw data for the analysis.

Introduction of the Fusion TOC Analyzer

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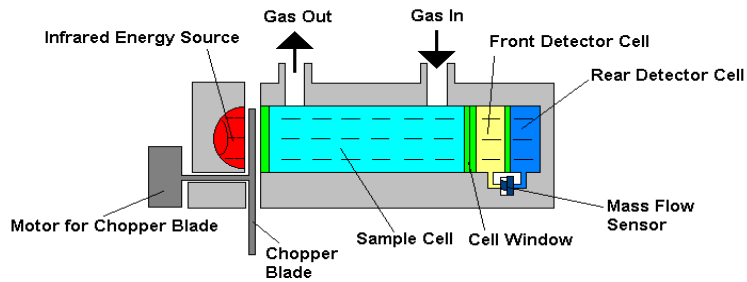


Figure 3 Phoenix 8000 flow through detector cell

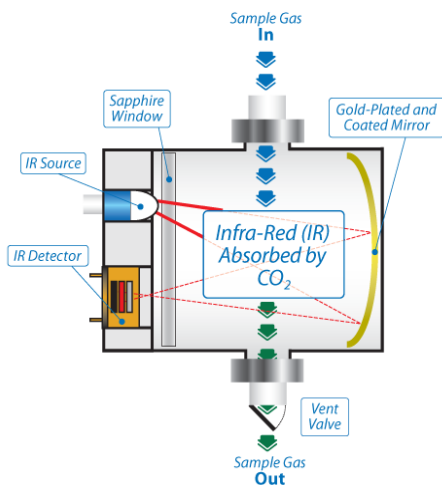


Figure 4 TOC Fusion detector cell

Anatomy of a SPC NDIR detector:

In contrast to an analyzer using a flow-through cell detector, the Fusion utilizes pressurized detection, or static read (figure 4). In this technique, oxidation of the specific carbon component and its movement, using a non-interfering carrier gas, into the detector is identical. However, the static read detector pressurizes the detector cell by closing the outlet valve and takes a single measurement to determine the amount of CO₂ inside the detector cell. This single reading correlates directly to the concentration of the carbon contribution from the sample.

The static read detector (figure 6) uses no moving parts to measure carbon dioxide. Inside the detector, a miniature lamp produces an electronically pulsed infrared beam. A mirror reflects the beam and re-focuses it back to an IR detector. Behind a silicon-based Fabry-Perot Interferometer (FPI) is the IR detector. The tuning of the electronics of the miniature FPI is so that its measured wavelength converts between the absorption bandwidth of CO₂ gas and a reference bandwidth. When the FPI passband coincides with the absorption wavelength of the CO₂ gas, the IR detector experiences a decrease in the light transmission. The measured wavelength of the FPI changes to the reference band (that has no

absorption lines) and the IR detector experiences a full light transmission. The degree of light absorption in the gas, indicated by the ratio of these two signals, is proportional to the gas concentration. As stated earlier, carbon dioxide shows a unique adsorption spectrum when infrared energy passes through it, allowing any NDIR detector to distinguish it from other gases (figure 5).

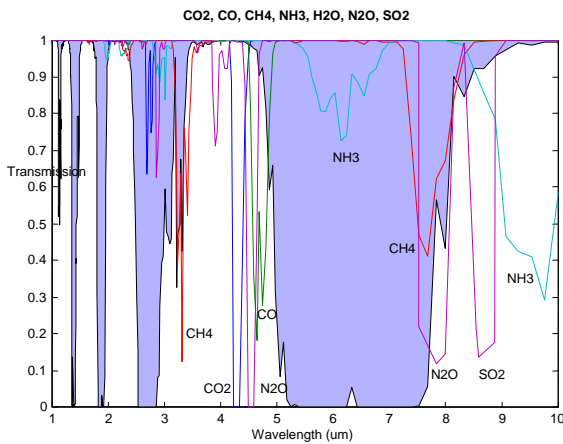
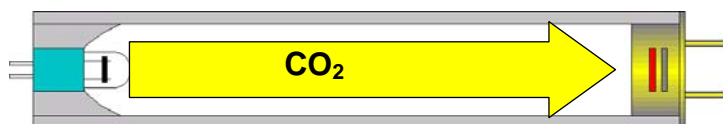


Figure 5 Absorption spectra for selected gases

The tungsten light source sends a single beam through the CO₂ gas. This beam reflects off a gold plated mirror to the detector. The Fabry-Perot Interferometer filters the light beam at an absorbance wavelength of 4.3 microns, which is specific for CO₂. A second beam is then sent and filtered at an absorbance wavelength of 3.9 microns, which is non-specific for CO₂. The difference between the absorbance readings is The Fabry-Perot Interferometer is silicon-based micro-machine (semi-conductor). They apply an electrical current to the semi-conductor and are able to tune (select) different absorbance wavelengths. The detector is a Thermopile (a thermocouple), which measures the heat potential and turns it into an electrical signal.

IR detector



Light source
with reflector

Sample cell

FPI detector

Hermetically Sealed Cap



Tunable FPI filter

An inherent advantage of this technique is that all of the CO₂ is in the cell at the same time for the detector to measure. This allows the sensitivity of the analysis to be significantly increased. In addition, static read detection does not have inherent error associated with integration inaccuracy (figure 6). The elimination of this error allows for lower detection limits and increased precision.

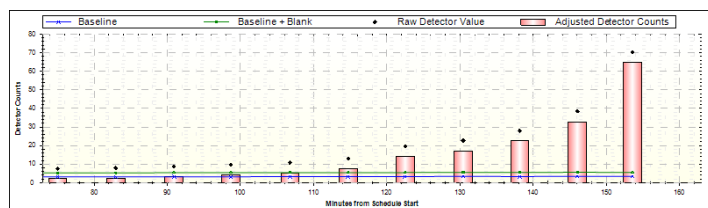


Figure 6 Typical Static Pressure Concentration (SPC) read display

Instrument Software

Software is in a user-friendly Windows format design. From the main instrument setup screen, access to nearly every function of TOC TekLink™ is available. The main window appears initially as a grey box. Five main dialogue boxes can toggle ON/OFF into the main window according to user preference. There is also the Unit Status window, an Event Dialogue window, and a Status bar at the bottom, which shows the mode and the connection status.

On the Unit Status window are various details of the analytical mode, instrument status, and zones, including flow rates, pressures and error messages. A Sample Information window, a real time NDIR signal chart, and a recent history of results are all displays within the Run screen. Sample Setup allows the user to enter relevant information about the sample ID, type of analysis (sample, calibration, blank, etc.), method of analysis (TOC, TC, IC, TC-IC) and the number of repetitions performed per sample.

The Tools menu contains many useful components. From the Tools dropdown box the Maintenance Tasks, Blank Editor, Standard Editor, Diagnostics, Update Firmware, System Properties, User Manager, and Change Password functions are available. One of the most helpful maintenance tasks is the Leak Check function. This permits pressurization of the flow path and ensures flow path integrity when the system is under pressure. Unlike the Phoenix 8000, the Fusion performs a single system blank. The

instrument blank screen displays the latest blank version and a View History button of the previous system blanks.

The Standard Editor accesses the list of standard sets previously created and controls the addition of new standard sets or the editing of existing ones. System suitability criteria can be set here as well. When creating or modifying a standard set, the user may choose to use the center autosampler positions for the stock standards or traditional 40mL vials. Using the same calibration file for multiple ranges or modes with TOC TekLink™ software is allowable.

The Diagnostics submenu permits manual control of the instrument valves, seven port valve and syringe drive, autosampler diagnostics, instrument benchmark, software debug, and Mass Flow Controller.

Chemistry of Oxidation and Analysis

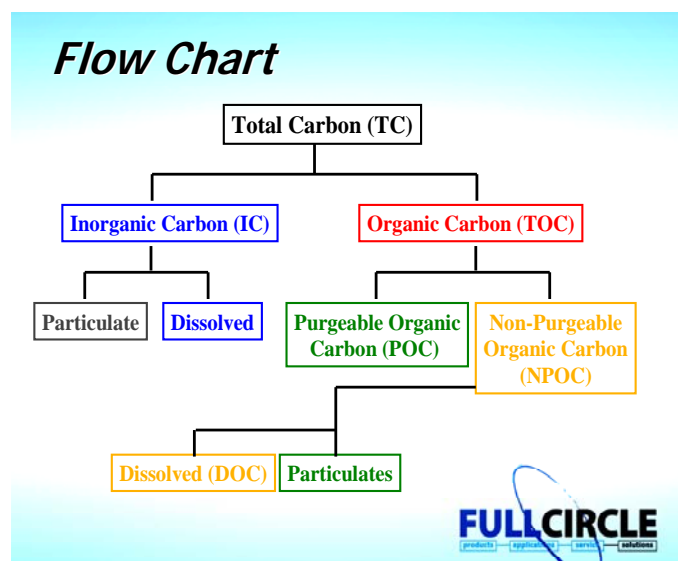
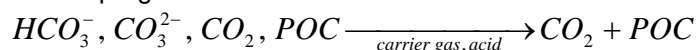


Figure 7 Carbon analysis diagram

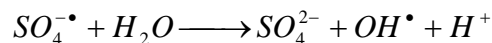
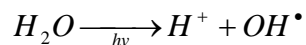
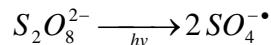
To determine TOC by the NPOC method, the Fusion transfers the sample and reagents to its reactors by first removing inorganic carbon, then oxidizing the carbon in the sample, and finally releasing it in the form of carbon dioxide. It then uses a carbon-free carrier gas to transfer the CO₂ from the sample to the NDIR detector in the following sequence:

1. Removal and venting of IC and Purgeable Organic Carbon (POC) by acidification and sparging in the IC sparger

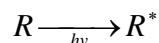


2. Following IC removal, an aliquot of the sparged sample is transferred to the UV Reactor and persulfate reagent is added to oxidize the organic carbon based on the following chemical reactions:

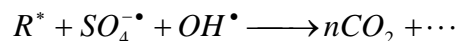
Free radical oxidants formed:



Excitation of organics:



Oxidation of organics:



Once the oxidation products in Step 2 are in the NDIR detector via the inert carrier gas, the pressure inside the detector rises to a predetermined set point by closure of the exit valve. The unique single measurement methodology the Fusion uses takes place only after the gases reach equilibrium inside the detector cell. This pressurization of the sample gas stream inside the detector, a patent-pending technique, allows for increased sensitivity and precision compared to a flow-through cell detector, by measuring all of the oxidation products from the sample in one reading. The output signal is proportional to the concentration of CO₂ in the carrier gas from the oxidation of the sample.

Results and Discussion

The Fusion enables the analyst to use fewer calibration curves and check standards to analyze a wide selection of samples. The new TOC TekLink™ software allows for continual flow of analysis – from auto-calibration to analysis of samples in one continuous schedule. TOC TekLink™ processes and selects the most recent standards and updates the calibration curve. Acceptance criteria of the calibration curve such as r² value, y - intercept and slope may be implemented in combination or individually. All samples analyzed following the newly generated curve are then automatically applied to that curve.

Calibration and analyses of 0.5, 1, 5, and 10, mg C/L content was performed. The FUSION instrument parameters were set at the following levels:

- 4.0mL sample injection volume, 0.5mL acid volume, 0.6 mL reagent volume and a UV Reactor pre-rinsing volume of 4.0mL.
- The auto-calibration curve was made from deionized water, 1, 5, and 10 mg C/L using a 20-mg C/L potassium hydrogen phthalate (KHP) stock solution shown in Figure 8.

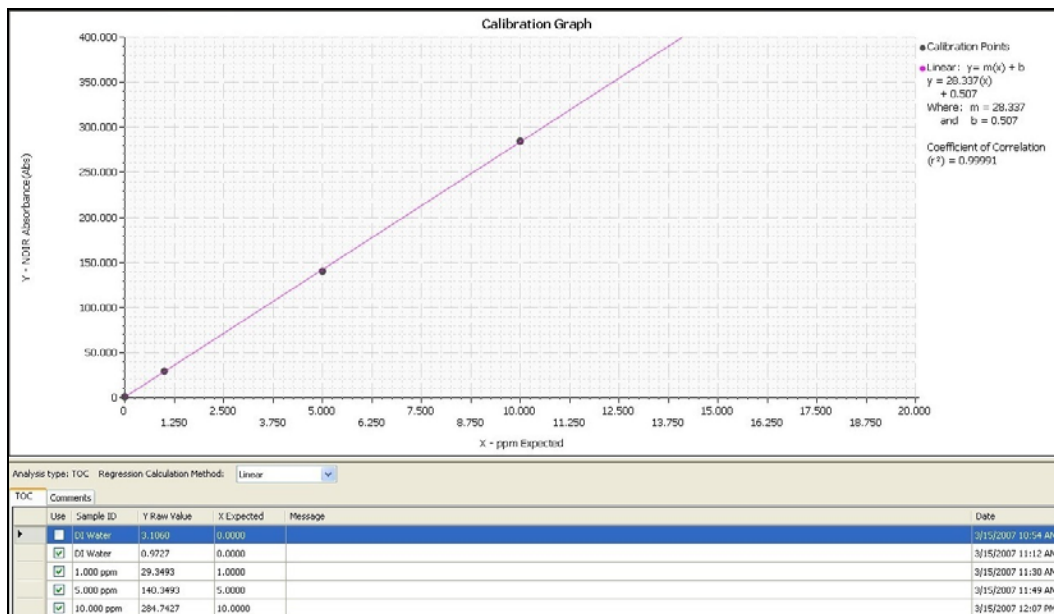


Figure 8 Fusion calibration curve

Sample Concentration (n=3)	Result (ppm TOC)	RSD
100 ppm	103.2512	0.16%
10 ppm	10.4552	0.34%
100 ppm	102.6462	0.20%
1 ppm	1.0048	1.60%

Carryover calculated by using a dilution method that did not over range the detector

Sample Concentration (n=3)	Result (ppm TOC)	RSD	Cross Contamination Carryover
1 ppm	0.9803	0.10%	N/A
50 ppm	34.5803	3.80%	N/A
1 ppm	1.1767	0.45%	0.57%
1 ppm	1.0691	0.59%	0.26%
1 ppm	1.0056	0.73%	0.07%

Table 2 Carryover calculated by using a non-dilution method to over range the detector

Two experiments demonstrate the ability of the Fusion to recover from analyzing high carbon concentration samples. The first uses the automatic dilution feature of TOC TekLink™. This feature allows the user to preset a method to dilute each 100 mg C/L sample to a predetermined concentration within the active calibration range (figure 8 and table 1). The major aspect of the carryover calculation is the effect of 100 mg C/L on the first replicate of the subsequent solutions between a ten and one hundred fold difference. The carryover for the 10 mg C/L 1 mg C/L samples is less than two percent. In the final experiment, the major aspect of the carryover calculation is the effect of 50 mg C/L, which will over range the linearity of the calibration curve by five fold, on low-level samples. The Fusion again demonstrates its superb capability to rinse the sample pathway in between samples as carryover is less than 1%

immediately following the out of linear range sample and two samples subsequently less than 0.1% carryover (table 2).

References

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The author thanks Eric Heggs and Stephen Proffitt for their invaluable input into this application note.