

## Application Note

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### **ABSTRACT**

The concentration of organic and inorganic carbon in seawater is of considerable interest. Some Total Organic Carbon (TOC) analyzers have been designed for straightforward analysis of these waters, with special features to avoid many of the problems found with salty samples. The presence of the chloride ion ( $\text{Cl}^-$ ) in waters being analyzed for carbon presents problems when the method uses low temperature oxidation of carbon-to-carbon dioxide. Such instruments typically use the persulfate ion with or without ultraviolet (UV) radiation. The  $\text{Cl}^-$  scavenges the free radicals that are the principal agents of oxidation, markedly reducing oxidation efficiency and prolonging oxidation time to an intolerable extent.

Complexation of chlorine by mercury ( $\text{Hg (II)}$ ) ion introduced into the reaction mixture reduces the chloride effect, but presents disposal problems for the spent reactor fluid. Further, the ( $\text{Cl}^-$ ) is oxidized to chlorine, which can damage the instrument's detector. Therefore, the low temperature UV-persulfate oxidation TOC analyzers are typically not advised for these salt-water applications without special reagent mixtures. With High Temperature Combustion (HTC) analyzers, the chloride ion does not affect the reaction rate and chlorine gas is not formed in high concentrations; therefore, historically these analyzers have been the instrument of choice for this application. However, the sodium ion does have a devitrifying effect on quartz glassware, which worsens with increasing temperature. Sodium chloride ( $\text{NaCl}$ ) also fuses onto catalyst at high temperatures, impairing oxidation efficiency, and is difficult to remove.<sup>1</sup> With persulfate oxidation based TOC analyzers, sodium and other cations do not interfere with the analysis.

### **Oxidation Technology**

#### High Temperature Combustion

The HTC technique uses heat usually in the presence of a catalyst, with a stream of hydrocarbon free compressed air to oxidize organic carbon. Dissolved organics and particulate organics are expected to oxidize fully to carbon dioxide under these conditions. HTC instruments may use a variety of different catalysts including cupric oxide, cobalt oxide or titanium dioxide based platinum. HTC oxidation requires temperatures from 680°C to 1000°C depending upon the application.

UV/Persulfate: Persulfate oxidation is a chemical oxidation aided by UV radiation and persulfate. This technique characteristically produces higher instrument responses versus background responses thereby yielding lower limits of detection in contrast to HTC oxidation.<sup>2</sup>

### **Detection**

All of the oxidation techniques form  $\text{CO}_2$  from the carbon in the sample. Detection of  $\text{CO}_2$  is accomplished by either:

- 1) **Conductivity / Membrane Conductivity** - allowing it to permeate a membrane into a low conductivity water stream and thereby change the water stream's conductivity
- 2) **Non-Dispersive Infrared** - purging the  $\text{CO}_2$  to an NDIR detector.

Conductivity/ Membrane Conductivity: The conductivity of the sample is measured before and after it is oxidized attributing this differential measurement to the TOC of the sample. During the sample oxidization phase,  $\text{CO}_2$  and other gases are formed. The dissolved  $\text{CO}_2$  forms a weak acid, thereby changing the conductivity of the original sample proportionately to the TOC in the sample. It is assumed that only  $\text{CO}_2$  is present and, if true, the TOC of the sample may be validated by calculating by the differential measurement.<sup>3</sup> Therefore, the conductivity measurement is an indirect measurement of the  $\text{CO}_2$  in the sample. The advantage of this technique is its sensitivity in pure water applications. However, the disadvantage of this technique is the fact that other ions within the sample matrix may

pass across the membrane into the pure water stream. Thus, the conductivity measurement may be influenced by the interferences.

**NDIR Detection:** NDIR detectors use infrared (IR) energy to detect the presence of CO<sub>2</sub>. Generally, an IR beam is transmitted through the empty sample cell to establish a baseline. A second IR beam is transmitted as the sample cell fills with CO<sub>2</sub> gas. When IR energy passes through CO<sub>2</sub> gas, it creates a unique adsorption spectrum differentiating CO<sub>2</sub> from other gases. Both IR beams transverse an optical filter allowing light of a predetermined wavelength (4.26µm) to reach the detector. A mass flow sensor connects pressurized front and rear cells. Changes in gas flow to the cells changes the pressure within each cell individually, which occurs as the detector fills with sample CO<sub>2</sub> gas. This pressure difference is detected by the mass flow sensor that emits an electrical signal proportional to the magnitude of the flow. As this occurs, the instrument monitor displays a single point on a graph corresponding to the emitted electrical signal usually in millivolts (mV). This point represents the amount of CO<sub>2</sub> inside the detector only at that particular moment. Illustrated together in Figure 1, the plotted points relate to the traditional flow-through cell bell shaped curve. As the adsorption of infrared light is measured over time, the CO<sub>2</sub> sample result is calculated by the mathematical integration of the area underneath this curve. There is no other detection scheme that offers a more practical, interference-free method for detecting CO<sub>2</sub> in TOC analysis than NDIR analysis. This technique measures the CO<sub>2</sub> in the gas phase, eliminating the interference effects of other compounds that remain in the sample.<sup>4</sup>

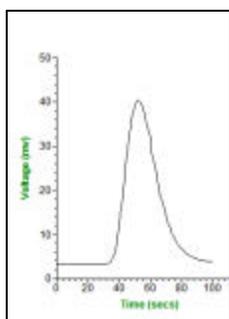


Figure 1. A display of the mathematical integration of a CO<sub>2</sub> peak or normal curve of error.

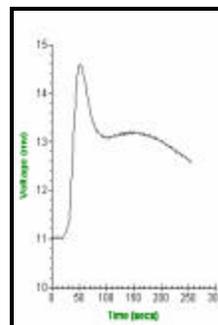


Figure 2. A display of halide interference on a traditional UV/Persulfate NDIR analyzer.

**The Fusion's Static Pressure Concentration NDIR Detection:** Similar to flow through cell NDIR detectors, the Teledyne Tekmar Fusion's Static Pressure Concentration (SPC) NDIR detector contains an IR light source and an optical filter. The CO<sub>2</sub> is swept into the detector and measured. Unlike other detectors, the path flow is pressurized driving the CO<sub>2</sub> into the detector where the exit valve is closed. Once all of CO<sub>2</sub> is inside the detector and pressure equilibrium is reached, an electronically pulsed light source emits a dual IR beam. Each beam is filtered by a Fabry -Perot Interferometer (FPI) that filters the light beams at an absorbance wavelength that is specific for CO<sub>2</sub> (4.26µm) and a nearby, non-absorbing wavelength used as a reference before being reflected and re-focused to the IR detector. The FPI is a micro-machined silicon chip that contains two parallel mirrors. The two parallel mirrors change distance when a voltage is applied over the chip, allowing only certain wavelengths of light to pass through to the IR detector. At the CO<sub>2</sub> absorption wavelength, the intensity of detected light is reduced in proportion to the concentration of CO<sub>2</sub> in the optical path. The light intensity measured at the non-absorbing wavelength serves as a baseline for comparison. 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 the NDIR to distinguish it from other gases. By regularly measuring CO<sub>2</sub> absorption and the reference band, the FPI can automatically compensate for light source intensity changes and loss of reflectivity of the optical sampling cell via contamination. This means that the NDIR detector itself can go for years without recalibration.

Additional advantages of SPC – NDIR detection are single measurement and no associated integration errors. One measurement represents the concentration of CO<sub>2</sub> in the cell versus multiple measurements

made in flow-through designs over time that result in a peak. Since this technique is a static read, it eliminates the inherent error associated with time delays between measurements. These time delays add error to the integration of the CO<sub>2</sub> peak. Most end users are unaware of the errors with the sample integration because of software smoothing and averaging of the peak integration. The Fusion's SPC – NDIR detection technology eliminates this error allowing for lower detection limits and increased precision.

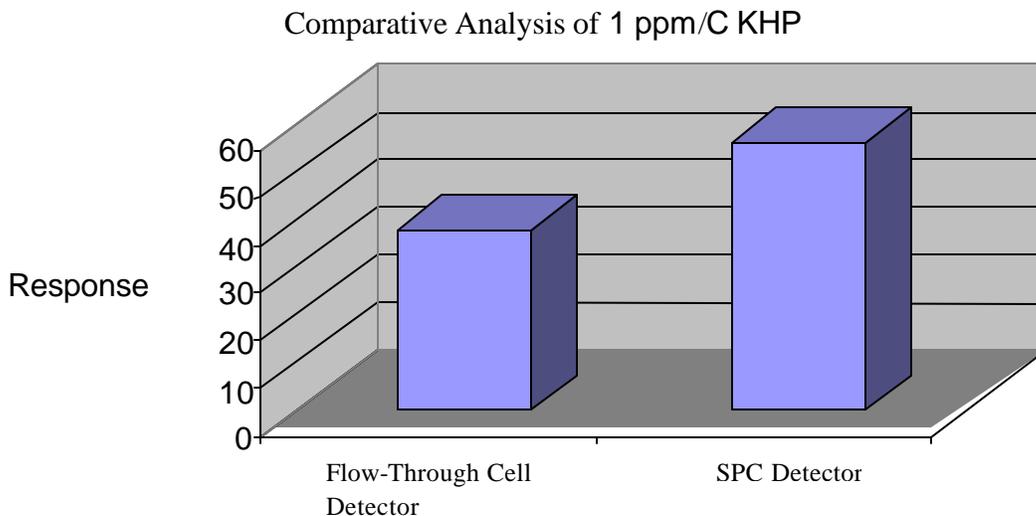


Figure 2. A comparison of 1 ppm/C Potassium Hydrogen Phthalate (KHP) results in instruments using NDIR detectors with traditional flow through and SPC – NDIR technology.

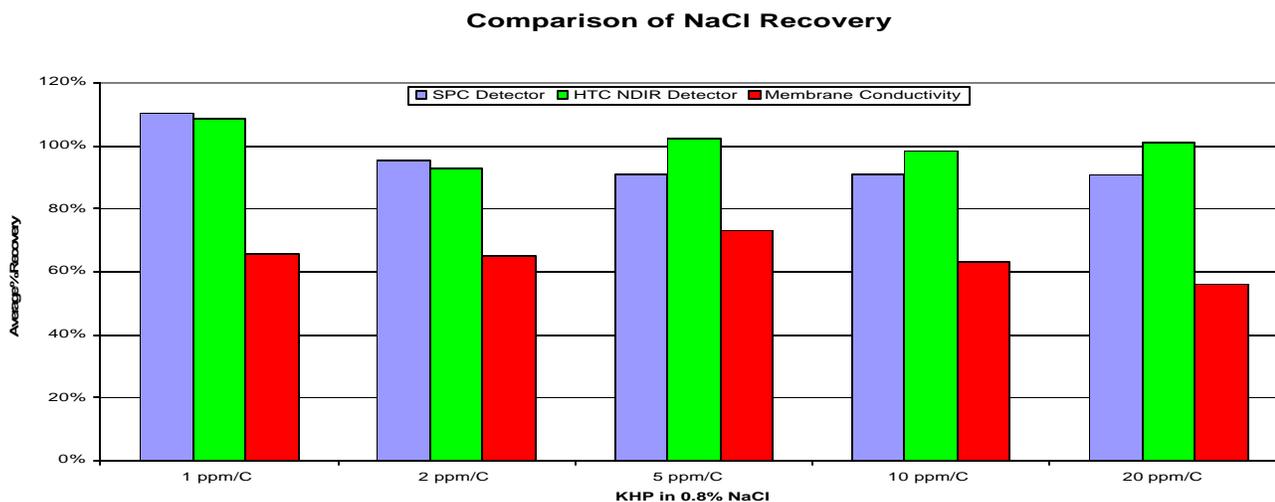


Figure 3. The Fusion UV Persulfate SPC analysis detection, high temperature combustion analysis detection and membrane conductivity detection comparison for TOC samples in 0.8% NaCl solutions. The NDIR detector technology demonstrates superior oxidation efficiency to the membrane conductivity detection technology for salt matrices.

NDIR Detector Type	Attribute
SPC Flow Through	Self-Calibrating Dual IR Beam Single IR Beam
SPC Flow Through	Fabry-Perot Interferometer Optical Filter
SPC Flow Through	Concentrated and Detection of CO <sub>2</sub> from analysis Smoothing / Averaging through Software Integration
SPC Flow Through	Automatic Leak Check on Every Sample Measurement of Flows Only
SPC Flow Through	Sensitivity & Flow Control

Table 1 Review of NDIR Detector Differences<sup>5,6,7</sup>

The pressurization of the entire sample gas stream using SPC-NDIR detector technology allows for:

- ◆ Increased sensitivity and precision compared to flow-through cell technology
- ◆ Dual beam vs. single beam – Reference wavelength can automatically compensate for light source intensity changes and loss of reflectivity of the optical sampling cell via contamination. Lower calibration and maintenance costs.
- ◆ Elimination of the inherent error that is associated with time delays between integrations included with traditional flow-through technology
- ◆ The Fabry-Perot Interferometer – Eliminates the optical filter that can experience contamination over time
- ◆ Solid State Detector – No moving parts compared to traditional NDIR detectors.

### Discussion

Many industries must analyze process and outfall water that contains salt. A catalytic combustion TOC analyzer provides one of the few ways of measuring TOC in brine solutions accurately. Other methods of oxidizing carbon experience severe interference from the presence of the high level of chloride ion. The new UV/Persulfate Fusion TOC analyzer using SPC-NDIR technology has introduced a revolutionary way to analyze waters containing levels of 0.8% sodium chloride, as seen in salt-water intrusion of surface and ground water sources. A comparative analysis of a high temperature combustion TOC analyzer using NDIR detection against the new Fusion UV Persulfate TOC analyzer using SPC NDIR detection demonstrates how effective the SPC technology is for the analysis of salty water, which can be seen in Figure 3.

### References:

1. Teledyne Tekmar Application Note, 'Measuring Carbon in Salty Waters, June 2003, TOC\_A-003.
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3. "The Conductivity of Low Concentrations of CO<sub>2</sub> Dissolved in Ultrapure Water From 0-100°C", T. S. Light, B. Kingman, A.C. Bevilacqua, 209th American Chemical Society National Meeting, Anaheim, CA, April 2-6, 1995.
4. Brian Wallace, Robert Stevens, "Evaluating Oxidation and Detection Technologies", *Pharmaceutical Formulation* March/ April 2004, 76 – 77.

5. Eric T Heggs, Edward K Price, Stephen R Proffitt, "CO<sub>2</sub> Measurements For TOC Analysis Using Static Pressure Reading of an NDIR" U.S. Patent
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7. Fusion Manual, Teledyne Tekmar 2007