

Applications Note

By: Stephen Lawson and Brian Wallace

The task of choosing a Total Organic Carbon (TOC) analyzer for cleaning validation and purified water testing brings one to consider the many techniques currently on the market. This becomes more difficult when faced with understanding that TOC analyzer manufacturers may use different detection techniques, which could affect the analytical data. This article highlights some analytical differences between the two major TOC detection techniques and offers suggestions for a process to base the choice upon the user's unique needs. A comparison of two commonly used techniques, Non-Dispersive Infrared (NDIR) and Membrane Conductivity, will be given based on sample matrices.

Background

Conductivity

The conductivity method, this includes direct and Membrane Conductivity, measures the conductivity of the sample before and after it is oxidized. The differential measurement is attributed to the TOC of the sample. During the sample oxidization phase, Carbon Dioxide (CO₂) (directly related to the TOC in the sample) and other gases are formed. The dissolved CO₂ forms a weak acid, thereby changing the conductivity of the original sample proportionately to the TOC in the sample. In this technique, it is assumed that only CO₂ is present and, if true, the TOC of the sample may be validated by calculating by the differential measurement. Depending on the chemical species present in the sample and their individual products of oxidation, they may present either a positive or a negative interference to the actual TOC value, resulting in commensurate analytical error.

TOC analyzers that employ direct conductivity detectors offer the simplest and most compact design available. However, over 50 ppm/C TOC conductivity measurements are not uniformly proportional to the TOC of the sample and vary widely with the specific carbon-containing species present, thus contributing significant error. ⁽¹⁾ The conductivity compensation errors involving temperature and TOC concentration are little known but are of significant importance. As it is often not practical to ascertain all the chemical constituents of an analyte and measure their effects, it is equally unlikely to derive a valid algorithm compensating for both the TOC "concentration" conductivity error and the error deriving from "temperature" effects, since conductivity temperature effects are also dependent on chemical and TOC concentrations. ⁽²⁾

Membrane Conductivity

A different approach to improving the accuracy of TOC analysis using conductivity has incorporated the use of hydrophobic gas permeation membranes to allow a more "selective" passage of the dissolved CO₂ gas to the "zero" water for subsequent conductivity analysis. While this has solved certain problems, membranes have their own particular limitations. Some of these limitations include clogging, true selectivity, and a location for secondary chemical reactions that are prone to promote "false negatives," a condition far more severe than "false positives" in critical applications. Micro leaks, flow problems, dead spots, microbial growth (blockage) are also potential problems. Certain amines will pass through membranes and add to the conductivity of the water loops. Most disconcerting is the inability of membrane methods to recover to operational performance after an overload condition arises that over-ranges the instrument. Often these instruments take hours before returning to reliable service and recalibration. Certain amines will pass through membranes and add to the conductivity of the water loops. Small changes in pH are also well known contributors to inaccuracy. The interference of the non-fully oxidized organics would remain, presenting both the error of incomplete oxidation and the consequent CO₂ detection interference.

NDIR Detection

NDIR detectors use Infrared (IR) energy to detect the presence of CO₂. An IR beam is transmitted through the sample chamber as the sample gas containing CO₂ fills the chamber. Pressurized front and rear cells connected by a mass flow sensor are located within the detector. An optical filter allows only light of a predetermined wavelength to reach the detector cells from the IR source. When IR energy passes through CO₂ gas, it creates a unique adsorption spectrum making CO₂ distinguishable from other gases. To collimate the IR light through the sample chamber and to increase optical efficiency, the light source is surrounded by a parabolic reflector assembly usually gold lined. Any change in gas flow to the cells changes the pressure within each cell individually. This pressure difference is detected by the mass flow sensor, which then 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 CO₂ inside the detector only at that particular moment. As the adsorption of the infrared light is measured over time, the amount of CO₂ inside the detector increases and decreases as the sample gas flows through the detector. Displayed together the plotted points relate to the traditional flow-through cell bell shaped curve. The CO₂ sample result is calculated by the mathematical integration of the area underneath this curve. The NDIR detection technique offers a more practical, interference-free method for detecting CO₂ in TOC analysis. This technique measures the CO₂ in the gas phase, eliminating the interference effects of other compounds that remain in the sample.⁽³⁾

Static Pressure Concentration (SPC)

Like flow through cell NDIR detectors, an SPC-NDIR detector contains an IR light source and an optical filter. However, unlike other detectors, as the oxidation products are swept into the SPC detector the inlet valve is closed allowing pressurization to occur. Once the gases inside the detector have reached equilibrium at a predetermined pressure setting, a Tungsten light source emits a single IR beam through the CO₂ gas. This beam reflects off a gold plated mirror to the detector. Prior to reaching the detector, a Fabry-Perot Interferometer (FPI) filters the light beam at an absorbance wavelength that is specific for CO₂ at 4.3 microns (μm). Under pressure and at equilibrium all of the CO₂ is then analyzed. The pressure required for static read is typically between 30-60 psig and defined in programmed methodology.

Inside the SPC detector is a thermopile, which is a temperature sensor. It turns thermal energy into an electrical signal. After the CO₂ is evacuated, the same Tungsten light source sends a second beam towards the detector. This second beam is the reference beam. The FPI filters that beam at an absorbance wavelength of 3.9 μm, which is non-specific for CO₂. The thermopile measures the difference between the signal of the infrared beam that has adsorbed CO₂ and the reference beam. This difference corresponds to the amount of CO₂ inside the detector and thereby the sample aliquot, as seen in Figure 1. The Fabry-Perot Interferometer is a silicon-based micro-machine (semi-conductor). When an electrical current is applied to the semi-conductor, different absorbance wavelengths can be selected. This in turn, allows different regions of infrared spectra to be chosen for absorbing and non-absorbing CO₂ regions.

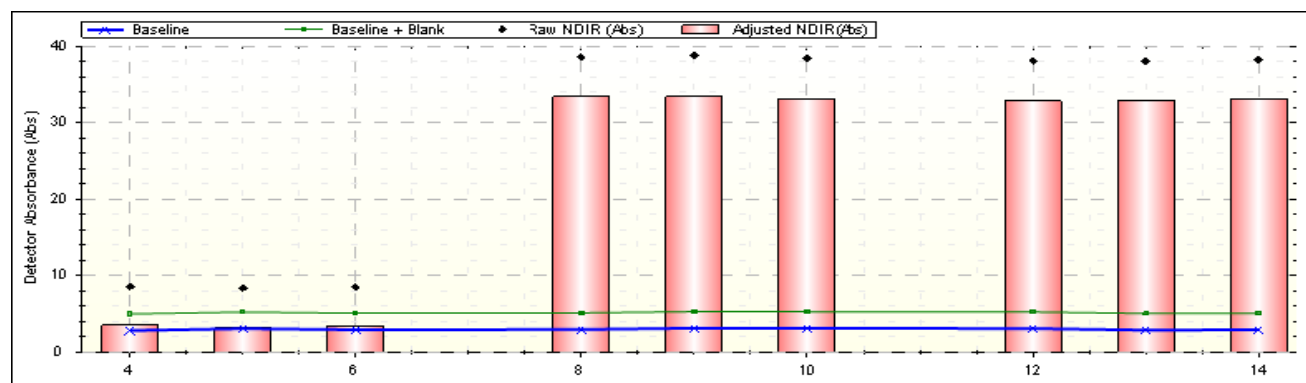


Figure 1 A display of CO₂ from a NDIR detector Static Pressure Concentration (SPC) detector technology, as used in the New Teledyne Tekmar Fusion TOC Analyzer.

Detection Selection for TOC Analysis:
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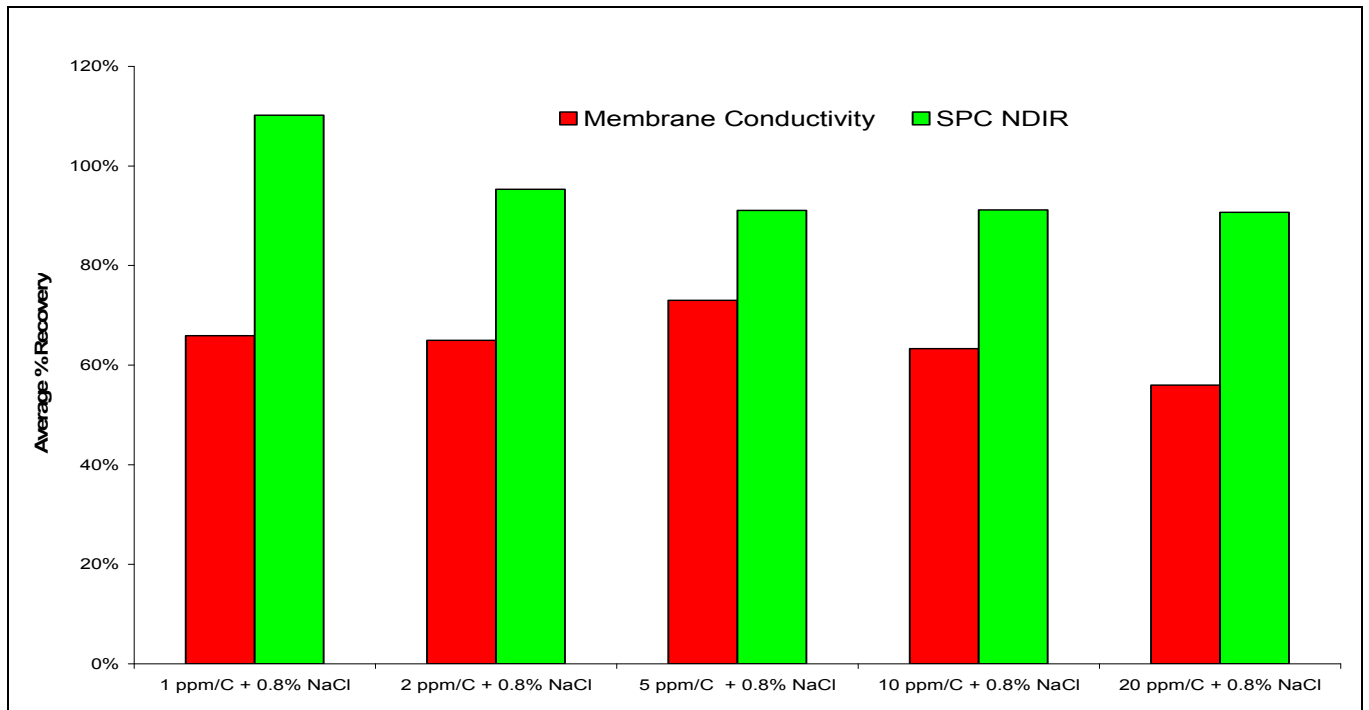


Figure 2. A comparison of Two TOC Analyzers using Membrane Conductivity vs. SPC-NDIR Detection Technology for analysis of TOC in 0.8% NaCl at increasing TOC concentrations. Each analyzer was calibrated to its manufacturing specifications prior to analysis.

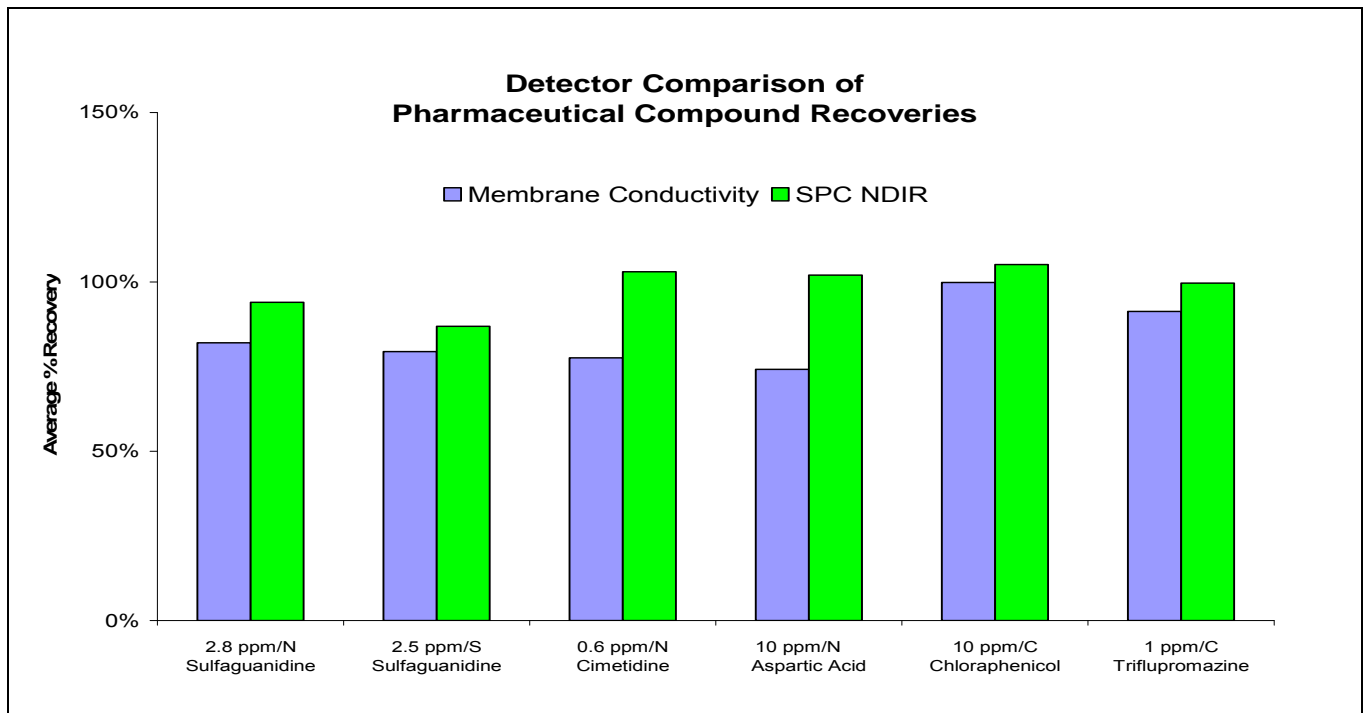


Figure 3 A Comparison of Pharmaceutical Compounds using Membrane Conductivity vs. SPC-NDIR Detection Technology. Each analyzer was calibrated to its manufacturing specifications prior to analysis.

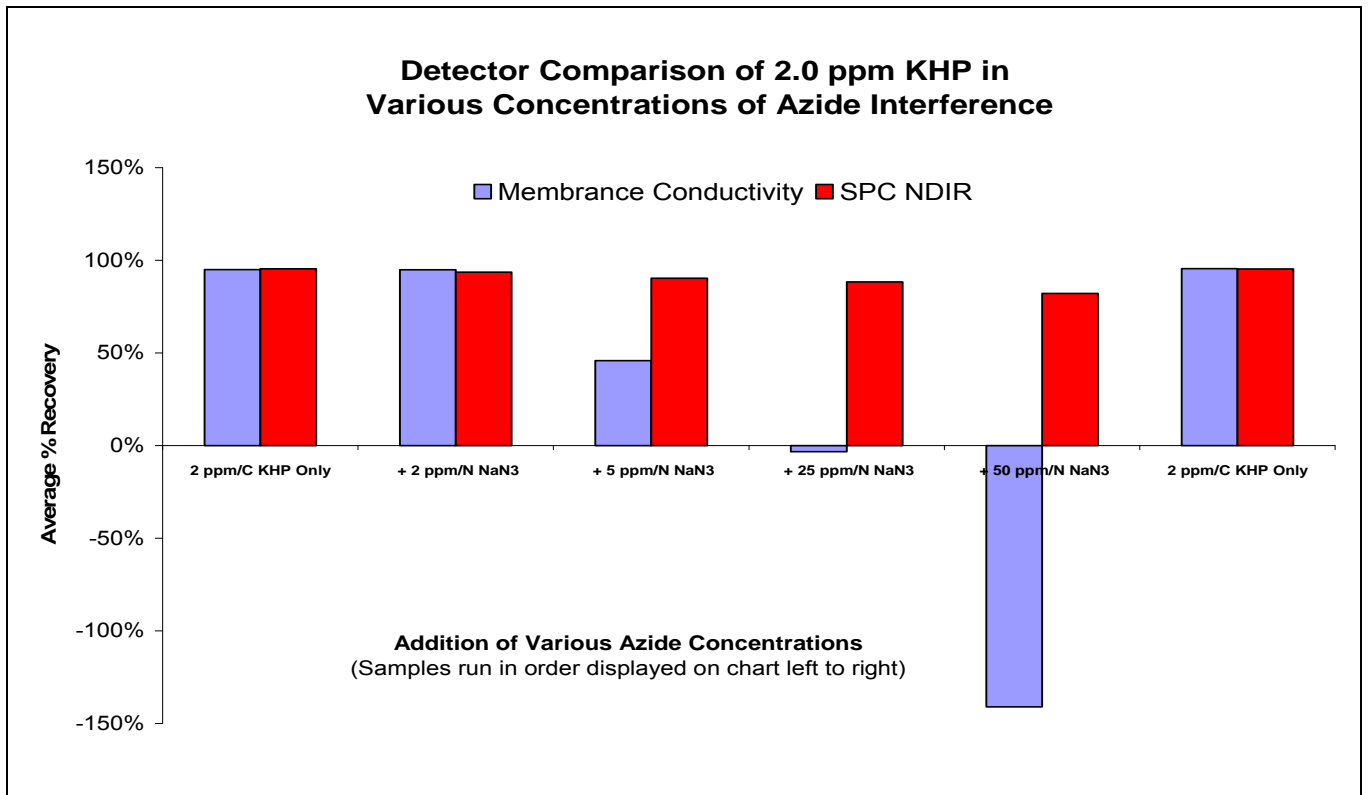


Figure 4. A Detector Comparison of TOC Analysis with Increasing Amounts of Azide present in an aqueous sample. Each analyzer was calibrated to its manufacturing specifications prior to analysis.

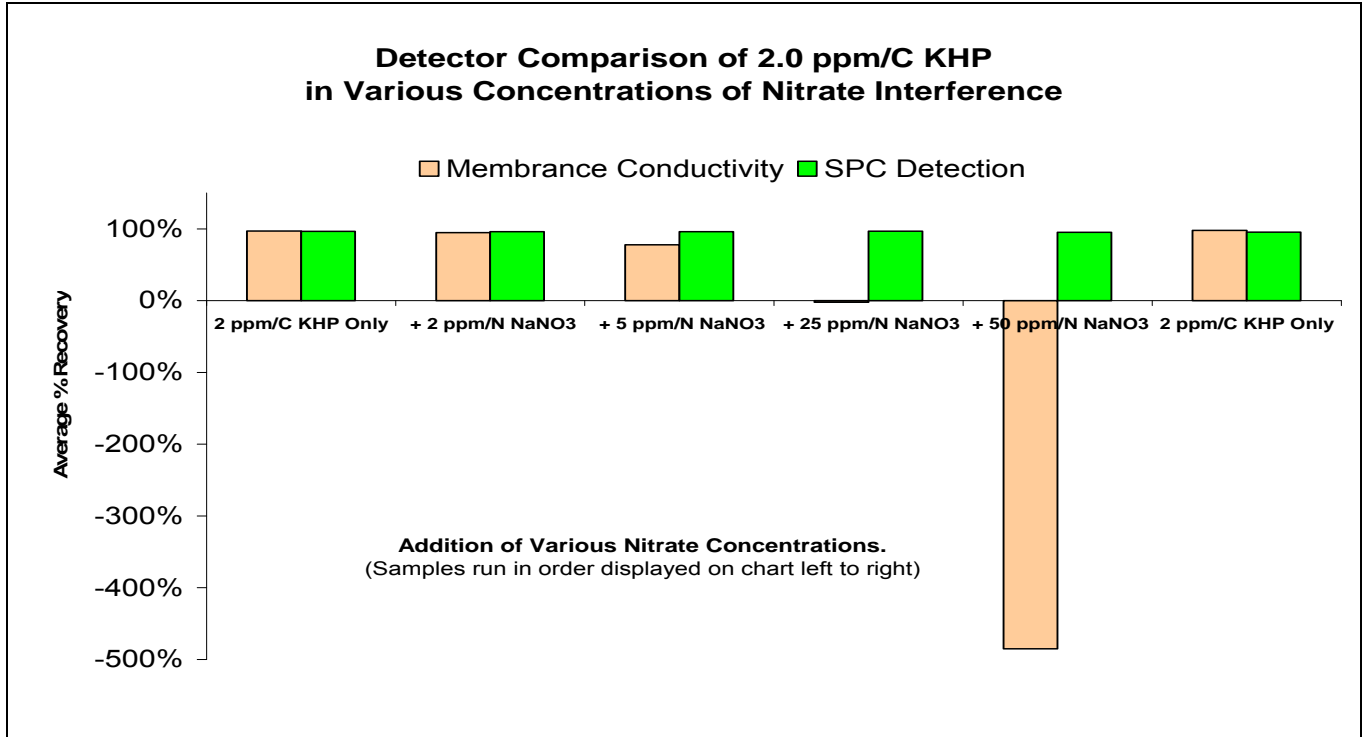


Figure 5. A Detector Comparison of TOC Analysis with increasing amounts of Nitrate Compounds present in an aqueous sample. Each analyzer was calibrated to its manufacturing specifications prior to analysis.

Conclusion

A comparison of brine sample analysis at a concentration of 0.8% sodium chloride shown in Figure 2, demonstrates the effectiveness of proven UV /Persulfate technology combined with SPC-NDIR detection. In contrast, SPC-NDIR technology by far surpasses the ability of membrane conductivity technology to analyze brines. A comparison of hard to oxidize pharmaceutical compounds, due to their complex molecular structure and varying levels of nitrogen, sulfur, and carbon is shown in Figure 3. As illustrated, the membrane conductivity detector did not effectively recover these compounds as compared to the SPC – NDIR detector. In Figures 4 – 5, nitrogen chemical species in the sample and their individual oxidation product interfere negatively with the membrane conductivity TOC recovery, as the nitrogen concentrations increase.⁴ Whereas, the SPC – NDIR detection technology achieved superior recovery and accuracy for all compounds studied. As seen in this study, the SPC – NDIR technology offers the best TOC analysis performance in a wide range of sample water matrices.

References

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