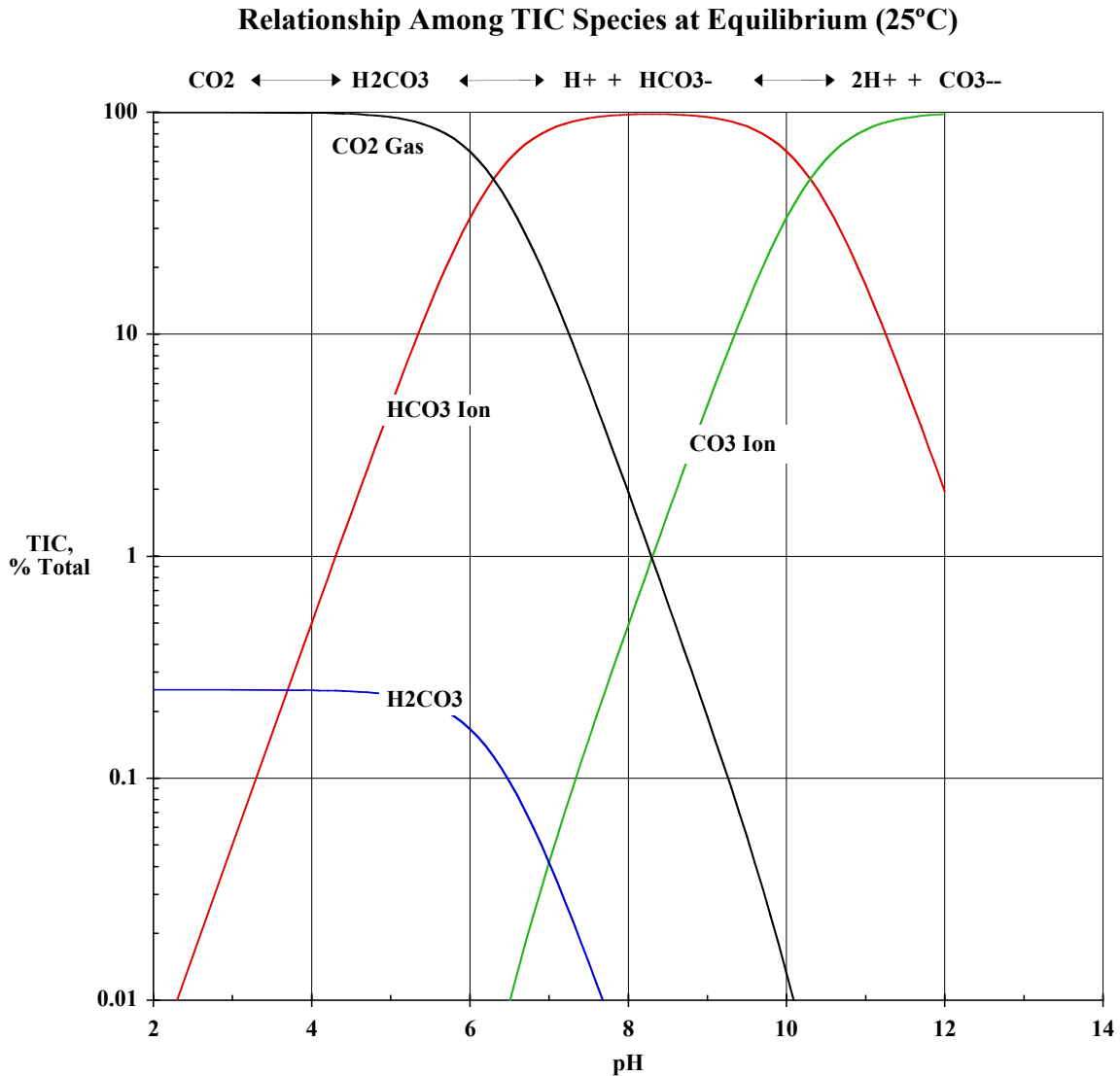


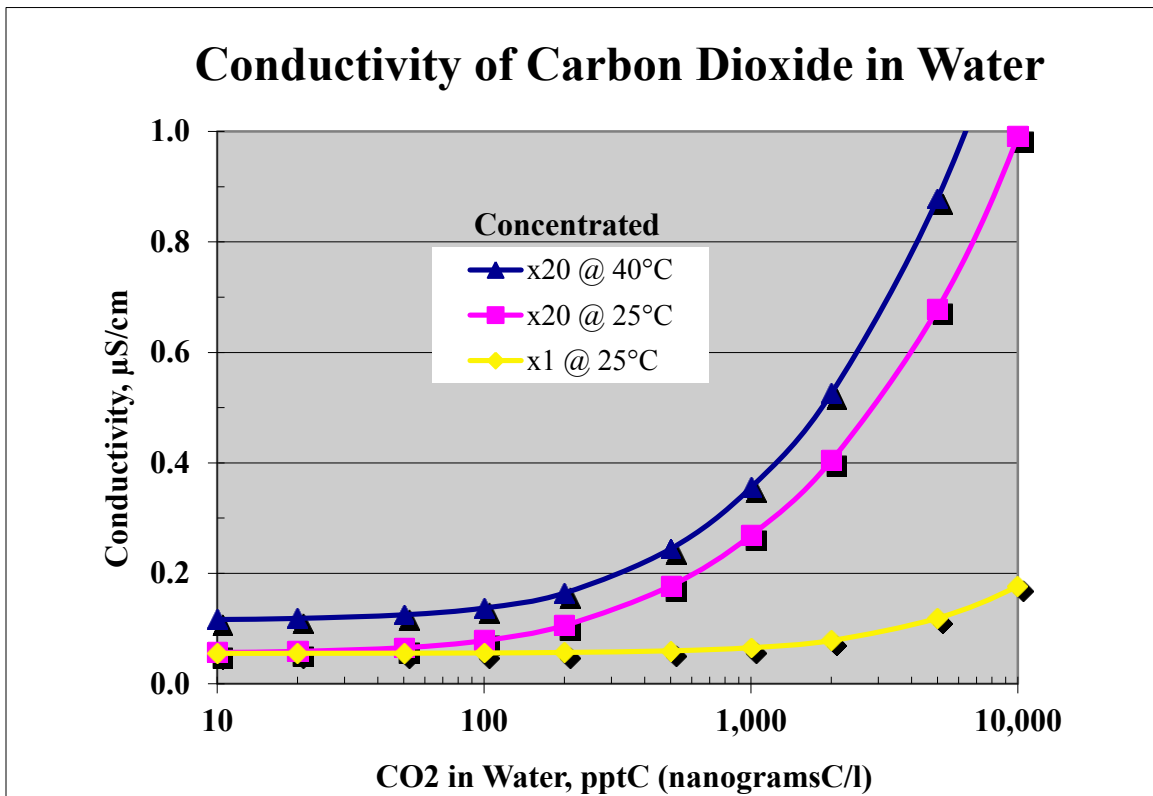
INTRODUCTION OF THE CO₂ CONCENTRATOR

Conductivity is a popular sensing technique for measuring the amount of CO₂ in water. The chart below illustrates the reactions occurring when CO₂ gas is absorbed in water. The ionic species....hydrogen ion (H⁺), bicarbonate ion (HCO₃⁻), and carbonate ion (CO₃⁼).... exist in equilibrium, which shifts with water temperature and pH. The conductivity sensor measures these conductive ions and its signal is used to compute CO₂ concentration, which is the sum of CO₂ gas, HCO₃⁻ ions and CO₃⁼ ions, using a chemometric model of the H₂O-CO₂ system.



However, when used for monitoring TOC the conductivity method is limited by the presence of ionic interferences such as inorganic acids, bases, salts, as well as ionic organic compounds, such as organic acids and bases, including ionic oxidation products. Comparative evaluations of available products has shown that those analyzers using direct inline CO₂ detection are plagued by both false-highs and false-lows because of these ionic interferences (References 1 and 2).

In addition, applications requiring low and sub-ppbC detection are limited by signal-to noise constraints. The figure below shows the increased sensitivity to CO₂ when concentrated by a factor of 20. Where a 5 ppbC (5,000 pptC) sample may be detectable without concentration, a 0.25 ppbC (250 pptC) sample can be detected with concentration.



A new unique technology which includes a CO₂ CONCENTRATOR has been developed to overcome the problem of interference which also significantly lowers the detection limit.

The CO₂ CONCENTRATOR shown below has two functions:

FUNCTION #1; Isolate ionic conductivity interferences from the CO₂ conductivity measurement. This eliminates the false-high and false-low problems associated with other instrument suppliers that measure CO₂ conductivity directly in the sample. One competitor separates the measured CO₂ from ionic interferences using a hydrophobic (gas permeable) membrane as the barrier. Conversely, the CO₂ CONCENTRATOR uses steam as the barrier. Ions do not travel in pure steam vapor as shown for decades by water purification systems using distillation. Ions only exist in liquid. CO₂ is transported with the steam while ionic interferences remain in the liquid.

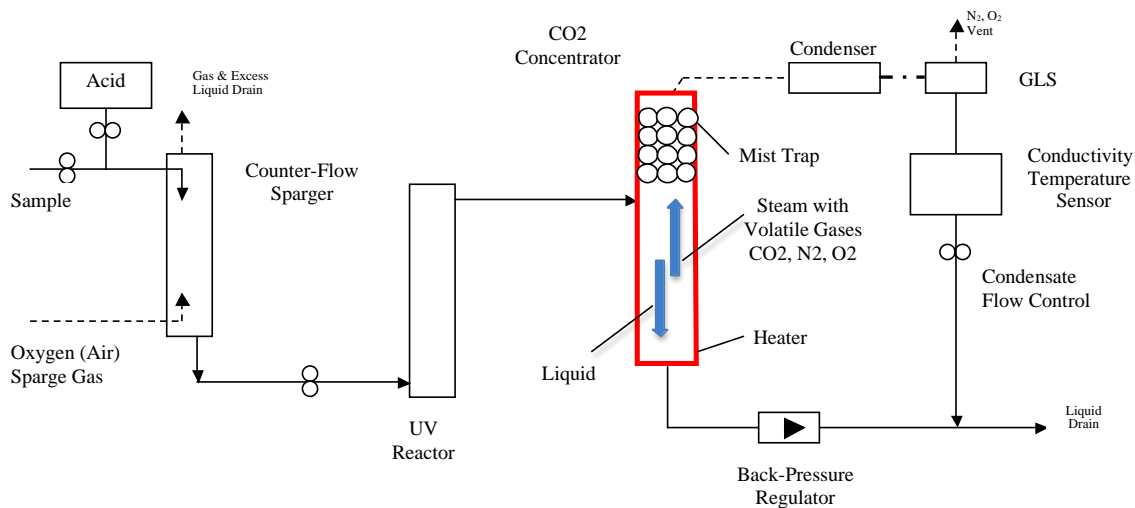
However, there can be entrained mist droplets that "contaminate" the steam, because they are liquid that may contain ions. The function of the MIST TRAP is to filter the droplets and return them back to the liquid.

FUNCTION #2; Concentrate the CO₂ in order to lower the MDL (Minimum Detectable Limit). The Concentrator releases the CO₂ from a relatively large volume of water while producing a much smaller volume consisting of steam which carries the CO₂ out the MIST TRAP. The CO₂ is recaptured in the small volume of condensed steam. This concentration factor allows improved sensitivity over the competition for ever-increasing demand for low-level TOC detection by the chip and pharmaceutical industries.

The potential benefit of improved sensitivity by concentrating is illustrated in the following table.

<u>Range, pptC</u>	<u>MDL (2% of Conductivity Range), pptC</u>		
	<u>No Conc</u>	<u>X20 Conc</u>	<u>X40 Conc</u>
10,000	391	87	61
1,000	156	28	20

CONCENTRATOR OPERATION DESCRIPTION



**Conceptual Schematic
TOC Instrument with Conductivity Detection of Concentrated CO₂**

Preheated sample from the UV reactor enters the CO₂ concentrator and flows down the heated tube wall where the water temperature is increased to ~100°C. The ullage is filled by desorption of gases... CO₂, O₂, N₂... from the liquid, along with a small portion of the vaporized sample water which acts as a CO₂ carrier. Liquid water continues down the heated tube wall of the BOILER to the bottom reservoir before exiting to the back-pressure regulator. The back-pressure regulator (check valve) supports vapor/gas flow out the upper MIST TRAP. Any excess water vapor produced by heating is condensed in the bottom section. An equilibrium exists at the operating pressure between vapor production by heating, condensation in the bottom section, and vapor/gas flow demand to the condenser.

CO₂ has only one possible exit...thru the MIST TRAP to the CONDENSER. With incoming sample flow of 5 mL/min and CONDUCTIVITY sensor flow of 250 µL/min CO₂ is concentrated X20.

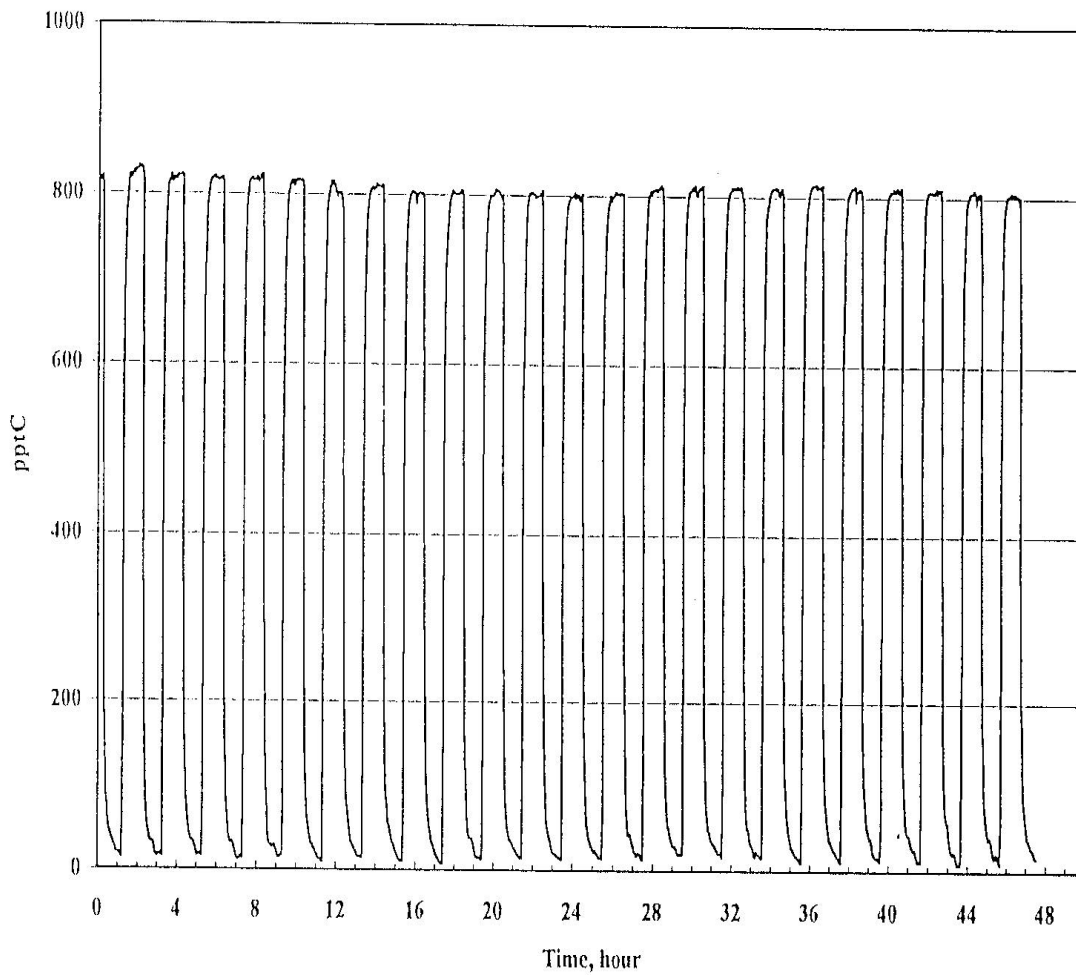
Vapor/gas flow thru the MIST TRAP is controlled by the condensate pump at the exit of the CONDUCTIVITY sensor. The trap is tilted so accumulated liquid mist does not obstruct vapor/gas flow to the condenser before it returns to the lower section. The MIST TRAP removes liquid entrained in the vapor to substantially eliminate all sources of ionic interference that would otherwise be carried over and contaminate the condensate.

The CONDENSER condenses the vapor carrier gas. CO₂ is then reabsorbed by the condensate. The GLS then removes the remaining atmospheric gases, O₂ and N₂, which

were released from the sample in the CONCENTRATOR. The conductivity sensor measures the CO₂ in the concentrated sample. Its signal is processed by the computer where the TOC present in the customer's sample is computed by the chemometric equations representing the CO₂-H₂O system.

PERFORMANCE

A prototype concentrator was tested by cycling the analyzer supply stream between a high (800 pptC) and low (0 pptC) concentration samples once an hour for a 48 hour period. The chart below shows the analyzer response with an average high sample reading of 804 pptC with a standard deviation of 5 pptC.



REFERENCES:

1. Donovan, R. P., et al, "Results From the Evaluation of On-line TOC Analyzers – Part 2, ULTRAPURE WATER, March 1999.
2. GE, "A Science Based Performance Comparison of On-Line TOC Analyzers.