

APLIKACIJSKI ČLANKI APPLICATION ARTICLES

Total Organic Carbon - TOC in Water Part I: Measurement and Instrumentation

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1.0 INTRODUCTION

The content of organic substances is an excellent indication of water quality. Monitoring of TOC - Total Organic Carbon - proved to be a fast, simple and reliable method of water analysis.

TOC monitoring systems are used in various industrial areas. The applications are process and waste water monitoring, high purity or cooling water analysis. Furthermore, TOC analysers can be applied to assess pollution levels in municipal waste water, drinking water, ground and surface water.

Table 1. Typical applications and users of TOC instrumentation

APPLICATIONS	USERS
Process water	Chemical industry
Waste water	Foodstuff industry
Cooling water	Power plants
Boiler feed water	Semiconductor industry
Reclaim water	Electronics industry
High purity water	Semiconductor and Pharmaceutical industry
Surface water	Paper industry
Ground water	Textile industry
Drinking water	Mineral oil refineries
	Airports
	Waterworks
	Sewage plants
	Research facilities

Traditional water quality parameters were COD (Chemical Oxygen Demand) and BOD (Biochemical Oxygen Demand).

For BOD measurement bacteria and nutrients are added to the water, and their consumption of oxygen is recorded, generally in mg/l of water.

On the other hand, for COD measurement, concentrated sulfuric acid and chromium are used to establish the maximum possible oxygen consumption of the sample. In the river Rhine in 1992 at the German - Dutch border, the BOD was measured at an average of three mg/l and the COD was 10 mg/l, /1/.

However, the laboratory measurements of these parameters are time consuming and not suitable for the quality control. On-line versions of COD and BOD monitors are available, but very expensive and not reliable.

TOC can offer cost - effective, quick and reliable monitoring. The TOC values can be correlated with the COD and BOD values if necessary. Of course, the relationship depends on kind of water pollution. As a rule of thumb: $COD = TOC \times 3$ and $BOD = TOC \times 1$.

In table 1 some applications and typical users of TOC instruments are shown.

2.0 CONVENTIONAL LABORATORY BASED METHODS FOR TOC ANALYSIS

TOC analysis methods were originally developed in the early 1960s to understand better the contents and treatment of drinking and waste water, /2/. Consequently, these methods were developed to detect high values of TOC. As the market expanded and more commercial suppliers offered instruments, variation of the original designs intended for lower concentrations appeared.

Analytical technologies utilized to measure TOC share the objective of completely oxidizing any organic molecules in a water sample to carbon dioxide (CO_2), measuring the resultant CO_2 level and then expressing this response as carbon concentration. Included in these techniques are combustion oxidation, flame ionization detection, wet oxidation using acid, persulfate and NDIR detection, calorimetric methods and aqueous conductivity methods.

2.1 Combustion Oxidation

The original combustion oxidation method measures total carbon (TC). It requires sample injection by syringe into a high temperature furnace with a platinum or cobalt catalyst. This process theoretically oxidizes all of the carbon materials to CO_2 which is directly propor-

tional to the organics present in the sample. Then, the CO₂ is swept into a non-dispersive infrared detector (NDIR) by a stream of dry nitrogen for final measurement.

A variation of this method employs a stream splitter which directs equal parts of the sample to two furnaces at different temperatures to measure the total inorganic carbon (TIC) at 150°C, and TC at 950°C. The TOC can then be calculated as:

$$\text{TOC} = \text{TC} - \text{TIC}$$

2.2 Flame Ionization Detection

Another early method for high TOC concentrations employs flame ionization detectors (FID) which reduce the CO₂ content to methane (CH₄). Sample oxidation requires the addition of sodium persulfate and a heated catalyst. Additional plumbing allows the volatile or purgeable organics to be measured. These systems are quite complicated and require hydrogen for the FID operation in addition to the acids, oxidants and carrier gases.

2.3 Wet Oxidation Using Acids, Persulfate, and NDIR Detection

The persulfate/NDIR methods are common in laboratory units. An acid is added to the sample water to reduce the pH to 2-3. At this low pH the inorganic carbon is oxidized to CO₂ and measured. All remaining carbonaceous compounds are assumed to be TOC. Persulfate is added, sometimes with heating and/or UV radiation, to expedite oxidation of the remaining organics to CO₂. The CO₂ which is directly proportional to the amount of TOC in the original sample, is then measured in an NDIR detector.

2.4 Calorimetric Methods

After sample acidification and sparging of the released CO₂ from inorganic carbon, persulfate is added in the presence of UV radiation to oxidize the organics in the sample water. The CO₂ produced passes through a semipermeable membrane and then is dissolved into a dilute, buffered phenolphthalein solution. The colour of this solution is sensitive to the pH changes caused by the process and is measured in a spectrophotometer at 530 nm.

2.5 Aqueous Conductivity Methods

CO₂, produced by the acid/persulfate oxidation with possible UV assistance, can be measured for conductivity changes after dissolution into ultra-pure water. The change in conductivity is a direct function of the TOC present in the water sample. In the addition to the reagents required, these methods must include an independent water system capable of producing theoretically pure water at 18.2 Mohmcm resistivity.

3.0 TOC IN ULTRAPURE WATER (UPW)

High-purity water has a very low conductivity (high resistivity). The theoretical specific conductance of "pure" water at 25 °C is 0.055 µS/cm (specific resistivity of this water is 18.15 Mohm-cm). When the conductivity of high purity water is measured at temperatures other than 25 °C only temperature compensation algorithms within microprocessor controlled instruments are adequate to provide reasonable estimates of the true conductivity at 25 °C.

TOC is present in high-purity water in very small amounts. TOC levels of less than 250 µg/l for PW (pharmaceutical Purified Water), 50 µg/l for WFI (pharmaceutical Water-for-Injection) and 10 µg/l or below (semiconductor UPW) are the norm in well controlled HPW systems. For these high-purity water TOC levels, the µg/l units are usually expressed as parts per billion (ppb). Semiconductor manufacturers have been already for a long time monitoring TOC in the HPW and many correlations with electrical parameters already exist. However, in pharmaceutical water only in near future the measurement of TOC is intended to replace the current USP oxidizable substance limit test for the detection of organic compounds.. TOC test is non-selective, sensitive, rapid, quantitative and highly reproducible. System suitability rather than a specific method of TOC analysis will be used to validate this measurement.

3.1 A TOC Analysis Method Designed Specifically for On-Line Process Monitoring

We have noted that recent trends favour the transition of laboratory analytical techniques to the on-line processes. Advantages include accurate trend information, continuous monitoring, early detection of potential upsets and, in many cases, reduced operational attendance resulting in lower costs.

In 1984, Anatel Corporation developed an advanced and patented method for measuring TOC in high purity water, /3/. This new technology, in addition to providing enhanced performance, was engineered into instrumentation designed specifically for on-line process monitoring. The equipment is reliable, rugged beyond the conventional standards of laboratory instrumentation, and provides detection limits for TOC that have never before been approached.

3.2 Operating Principle of the Anatel TOC Technology

As with most significant new technologies, its appeal lies in the elegant simplicity of the method, /4/. Anatel eliminates the need and inconvenience of reagents, gases, and heating devices to achieve full oxidation of organics in the sample water.

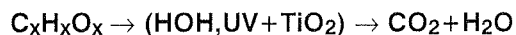
The instrument's compact design permits monitoring of each critical water purification component for optimal performance throughout the system. In on-line operation, a side stream of water is directed through the instrument's analysis cell for a user selected period.

During this *Sample Time*, the resistivity and the temperature of the water are measured and displayed continuously.

At the end of the *Sample Time*, the internal valve closes, "capturing" the water sample which is exposed to 185 nm UV radiation to begin oxidation. The optimally designed configuration of the UV lamp, quartz window, and reaction-enhancing titanium electrodes within the cell ensures efficient, complete, and reproducible oxidations.

The photocatalytic reaction produces hydroxyl radicals ($\bullet\text{OH}$) on the surface of the titanium electrodes. These $\bullet\text{OH}$ groups are strong oxidants and replace the persulfates that are needed in conventional instruments. This photocatalysis, along with a proprietary set of

sophisticated software algorithms for monitoring the reaction, assures complete oxidation of the organics.



The CO_2 which is produced during the oxidation process dissolves into the water and forms carbonic acid which dissociates into conductive ionic species:



The change in conductivity due to the dissolution of CO_2 into the water is directly proportional to the concentration of TOC originally present in the sample.

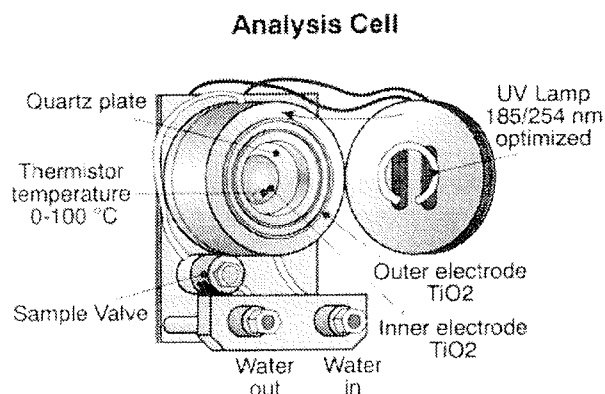


Figure 1: Schematic of the A-1000 Analysis Cell

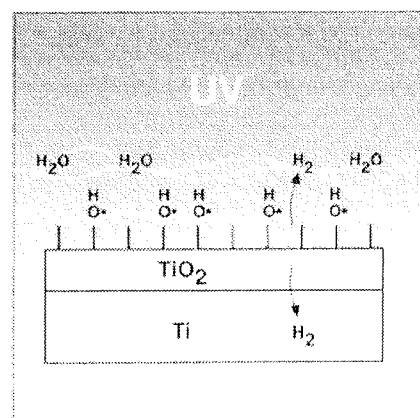


Figure 2: Photocatalytic production of hydroxyl radicals

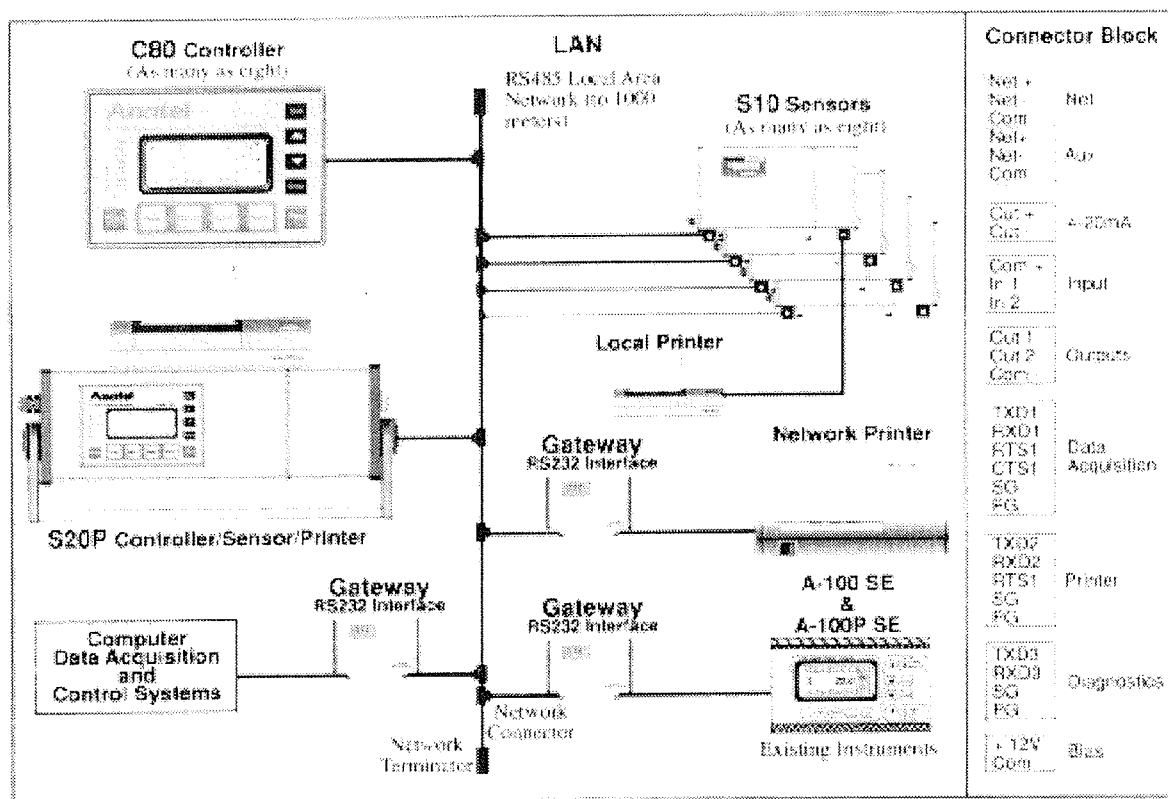


Figure 3: Schematic of the A-1000 network system with cable, connectors, connector block and multiple sensors

3.3 A-1000 Instrument Configuration

The minimum Anatel A-1000 TOC Analysis System combines a Controller and a Sensor unit. Multiple Controllers and Sensors may be linked together via a proprietary local area network (A-Net) to furnish a wide variety of potential system configurations. Possible applications include differential TOC measurements between two sensors.

C80 CONTROLLER

The C80 Controller serves as a control/display device for the A-1000 TOC measurement system. A 4-line by 16-character display presents information. Function and edit keys provide the ability to display and modify the various parameters which control the Sensor's operation.

S10 SENSOR

The S10 Sensor is the basic A-1000 analysis device. A 1-line by 16-character display reports current TOC values in ppb. Operation parameters for the S10 are established through a C80 Controller.

S20 SENSOR

The S20 combines the analytical and interface capabilities of the S10 Sensor with a C80 Controller. This union allows the control and reporting of the Sensor to be integrated into a single enclosure. The S20P Sensor's incorporation of an integral printer furnishes total instrument portability with point-of-use reporting capabilities.

3.4 A-1000 Operation Modes

The Anatel A-1000 TOC Sensors operate in one of five modes:

1. AUTO TOC

Auto TOC is the analysis mode for monitoring ultrapure water systems. The Sensor automatically performs successive measurements, reporting the TOC level, conductivity and temperature of the water stream at the end of each analysis cycle.

2. PURGE MODE

The Purge Mode opens the Sensor's internal solenoid valve, allowing water to flow through and flush the measurement cell. Conductivity and temperature readings are continually updated and printed either at user-selected time intervals or based on a change percentage as dictated by the instrument's operational parameters. The Purge Mode is used to check the sample water flow rate through the Sensor.

3. DIFFERENTIAL MODE

The Differential Mode is a comparison of two Sensors' Auto TOC or Purge Mode readings. A primary and a reference Sensor report their respective and differential measurements at the end of each analysis cycle.

4. MANUAL MODE

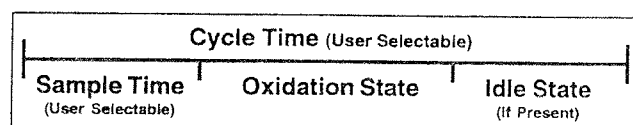
The Manual Mode allows the user to interrupt automatic operation and manually initiate an analysis cycle.

5. SELF-CLEAN MODE

In the Self-Clean Mode, the Sensor's solenoid valve is opened to allow water to flow through its measurement cell. The UV lamp is turned on to oxidize any organic contaminants, which are subsequently flushed from the cell by the water flow. Conductivity and temperature are reported as described in the Purge Mode.

3.5 A-1000 Auto TOC Mode Analysis Times And States

In the Auto TOC Mode, the A-1000's TOC analysis process is comprised of three stages: Sample Time, Oxidation State and Idle State—collectively referred to as the Cycle Time.



- **Cycle Time**
 - User Selected Times (minutes)
 - Comprised of 3 States or Times
 - Sample Time
 - Oxidation State
 - Idle State
- **Analyzer Rate**
 - Normal
 - Fast

Figure 4: A-1000 analysis cycle time line

1. SAMPLE TIME

During the user selectable Sample Time, the UV lamp is turned off and the Sensor's internal solenoid valve is opened to allow pressurized water from the process stream to purge the connecting tubing, valves and measurement cell. The Sample Time interval must be sufficient in duration to furnish a fresh and representative water sample for each measurement cycle. The required duration of the Sample Time depends on:

- the length and internal diameter of the sampling system's transfer tubing from the process pipe to the analyzer.
- the water flow rate.
- the difference between the ambient temperature and the temperature of the process water.

Typically, a Sample Time of two minutes is adequate at a flow rate of 100 ml/minute. The flow of water should be observed from the Sensor's WATER OUT port during the Sample Time interval.

2. OXIDATION STATE

During the first ten seconds of the Oxidation State, the conductivity and the temperature of the sample water are measured to establish reference values which are stored in the A-1000's memory for use in calculating the TOC results. The internal solenoid valve is then closed

to capture a fresh, discrete, representative water sample in the measurement cell. The UV lamp is turned on and oxidation of any organics within the sample occurs. The Oxidation State interval varies depending on the type and concentration of the organic constituents in the water and is characterized by Profile Types P1, P2 and P3.

The sample's final equivalent TOC content is calculated and based on the conductivity and temperature at the completion of the Oxidation State. The sample's TOC in ppb, initial conductivity ($\mu\text{S}/\text{cm}$) or resistivity ($\text{Mohm}\cdot\text{cm}$) corrected to 25 °C, and temperature (°C), are sent to the A-1000's display, analog and serial output ports.

3. IDLE STATE AND VALVE AT IDLE

If the TOC analysis is completed before the set Cycle Time has elapsed, the Sensor goes into an Idle State in which the UV lamp is turned off awaiting the start of the next analysis. During this Idle State, the internal solenoid valve is either "Open" or "Closed" as determined by the A-1000's Valve @ Idle setting. Open - the Sensor's measurement cell is continuously purged with sample water until the conclusion of the Cycle Time. Closed - the internal solenoid valve prevents water flow until the conclusion of the Cycle Time and initiation of the next Sample Time interval. The next analysis cycle begins immediately if the duration of the Cycle Time is less than the time required for complete sample analysis.

4. ANALYZER RATE

The A-1000's Analyze Rate determines the speed at which oxidation of the water sample occurs. "Normal" is the standard analysis rate. "Fast" performs the analysis up to three times quicker. The Fast rate is recommended only for applications where rapid results are crucial since prolonged operation on this setting reduces the life of the Sensor's UV lamp.

3.6. Oxidize state profile types

During the Oxidize State of the Auto TOC analysis cycle, the Sensor continuously monitors the changing conductivity and temperature of the water sample trapped in the measurement cell until oxidation of the organics is complete. The relationship between conductivity and time is called the oxidation curve. One of three oxidation curve Profile Types is reported by the A-1000: "P1," "P2" or "P3."

1. PROFILE TYPE 1 (P1) - Easy to Oxidize Organics

In a P1 sample, conductivity is always increasing until oxidation is complete. This profile indicates that only simple low molecular weight organics are present in the sample water.

2. PROFILE TYPE 2(P2) - Moderately Difficult to Oxidize Organics

The P2 sample occurs only at TOC levels below 25 ppb and is very similar to a P1 profile in which the contribution of the organic "background" of the cell must be adjusted.

3. PROFILE TYPE 3 (P3) - Difficult to Oxidize Organics

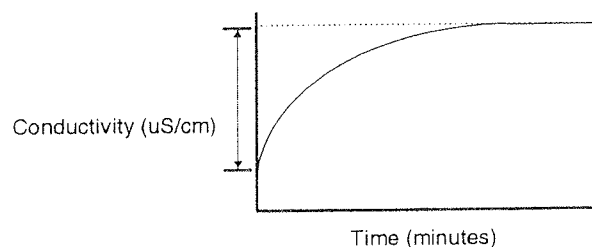
A P3 sample contains organic compounds which form significant amounts of intermediate organic acids which have a higher conductivity than the equivalent CO_2 that is finally formed. This produces an initial high level of conductivity which then decreases as the oxidation process proceeds to completion.

A change in Profile Type is an important information and usually indicates that something has happened within the water system. An abrupt change usually indicates a change in the organic content of the water. For example, a change from a P1 to a P3 Profile Type would result from the introduction of more complex organic compounds.

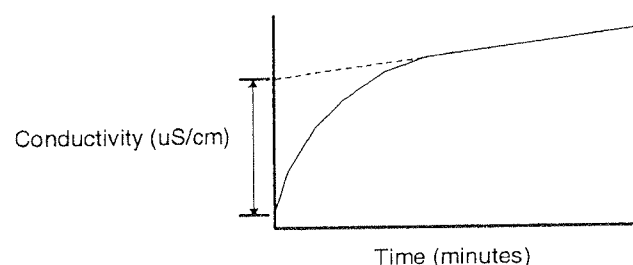
3.7 Alarms

The user may set an alarm limit for the TOC level that is detected by the Sensor. Any TOC limit excursions are indicated on the C80 Controller by the flashing of the entire LCD display as well as the affected Sensor's channel LED. When enabled, an audible beeper also sounds and, if connected, a hardcopy printout of the

Profile Type 1 (P1) - Easy to Oxidize Organics



Profile Type 2 (P2)



Profile Type 3 (P3) - Difficult to Oxidize Organics

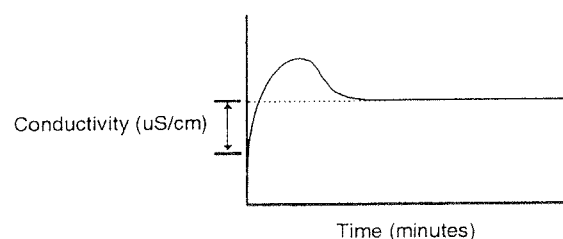


Figure 5: Oxidize state profile types

excursion is generated automatically. The Sensor's digital OUTPUT #1 port may be used to transmit the alarm to a compatible device. Alarms are acknowledged by pressing the (alarm) key on the C80 controller.

3.8 Errors

The C80 Controller is also used to display any Sensor malfunctions, reported as numeric Error Codes, indicating an electromechanical or analytical failure. The Sensor's channel LED and the Controller's display flash to alert the user of the problem and the error is acknowledged by pressing the (alarm) Key. Each Sensor maintains an error log of as many as 30 separate entries consisting of the Error Code number, the total number of occurrences of that error, and a time stamp of the initial occurrence.

3.9 Analyzer outputs

The A-1000 Sensor communicates to external devices through an RS-232C interface, 4-20 mA analog signals and digital output ports.

1. SERIAL OUTPUTS

An RS-232C port is provided to drive a printer or other serial communications device.

2. ANALOG OUTPUTS

Two types of ports are provided for signals to analog devices. The primary port provides a 4-20 mA signal which represents TOC. The secondary port is through the Sensor's DIAGNOSTIC port to allow the use of External DAC (Digital-to-Analog Conversion) modules to transmit 4-20 mA signals representing temperature and resistivity values. The minimum and maximum levels corresponding to the 4 and 20 mA signals may be defined by the user for TOC, temperature and resistivity. The user also may select one of three default output states for the analog signals should a fatal error be encountered by the Sensor.

3. DIGITAL OUTPUTS

The Alarm Status and the state of the internal solenoid valve are available on the Sensor's two digital output ports.

3.10 ANATEL - 1000 system specifications

SPECIFICATIONS	A1000
TOC	
Operating range	0.05 - 9999 ppb
Repeatability	better than $\pm 0.05 \text{ ppb} < 5 \text{ ppb}$ better than $\pm 1\% > 5 \text{ ppb}$
Accuracy	$\pm 1\%$

Display Resolution	0.00 - 19.99 ppb
	20.00 - 199.9 ppb
	200 + ppb
Minimum input water resistivity	5 Mohmcm for all water
	1 Mohmcm for neutral waters
	0.2 Mohmcm for water with CO ₂ as conductive species
Input water temperature	0 - 100 °C
Temperature measurement	YES
Input water pressure	15 - 100 PSIG max
Operating temperature	5 - 40 °C
RESISTIVITY	
Operating range	0.01 - 18.2 Mohmcm
	0.05 - 100 $\mu\text{S/cm}$
Temperature compensation	to 25°C over entire 0 - 100°C temperature range or temperature uncompensated resistivity
Readout resolution	3 significant figures as resistivity
	4 significant figures as conductivity
Precision	$\pm 3\%$
INPUT/OUTPUT	water IN/OUT
	AC plug
CONFIGURATION	Network RS-485 : 8 S10 sensors can be connected to C80
	Printer RS-232C
	Data RS-232C to computer!!
	Digital output (2) and input (2)
Calibration:	Against reference instrument
Validation:	According to USP 23
	IQ/OQ Guidelines and SOP available
Dimensions:	H325mm x W172mm x D112mm
	Weight 5.4 kg
MODEL	C80 Controller
	S10 Sensor
	S20: Controller + Sensor (portable)
	S20P: Controller + Sensor + Printer (portable)

4.0 The Anatel Model A-2000 for Wide Range TOC Analysis

The A-2000 is designed specifically to address higher range TOC analysis of feedwaters to high purity systems, clean-in-place applications in the pharmaceutical industry, reclaim and reuse water in semiconductor manufacturing, drinking water, power generation systems, chemical processing, and effluent streams.

The A-2000 TOC Analyzer offers four user-selectable analysis modes:

- TC - Total Carbon
- TIC - Total Inorganic Carbon
- TOC Direct and
- TOC Indirect

TOC measurements are made directly by sparging to remove any TIC present or indirectly by analyzing for both TC and TIC. The difference between these two measurements is the TOC value.

4.1 A-2000 Components

A-2000 system measures TOC by oxidizing the organic carbon to CO_2 with persulfate in the presence of ultraviolet light. The CO_2 produced is measured directly by a nondispersive infrared detector (NDIR). This method measures both the purgeable and non purgeable organic carbon that are present.

The main A-2000 components are:

High Efficiency Photoreactor

The high efficiency photoreactor consists of a hollow quartz tube, more than 1 meter length, wrapped into a helix just 2" long, encircling a 254 nm UV lamp. The tube, measuring just 3 mm in outside diameter and 2 mm in internal diameter ensures that the sample is always strongly exposed to penetrating UV energy for maximize oxidation performance. The long, small diameter quartz tube ensures fast, complete, UV promoted persulfate oxidation in just minutes.

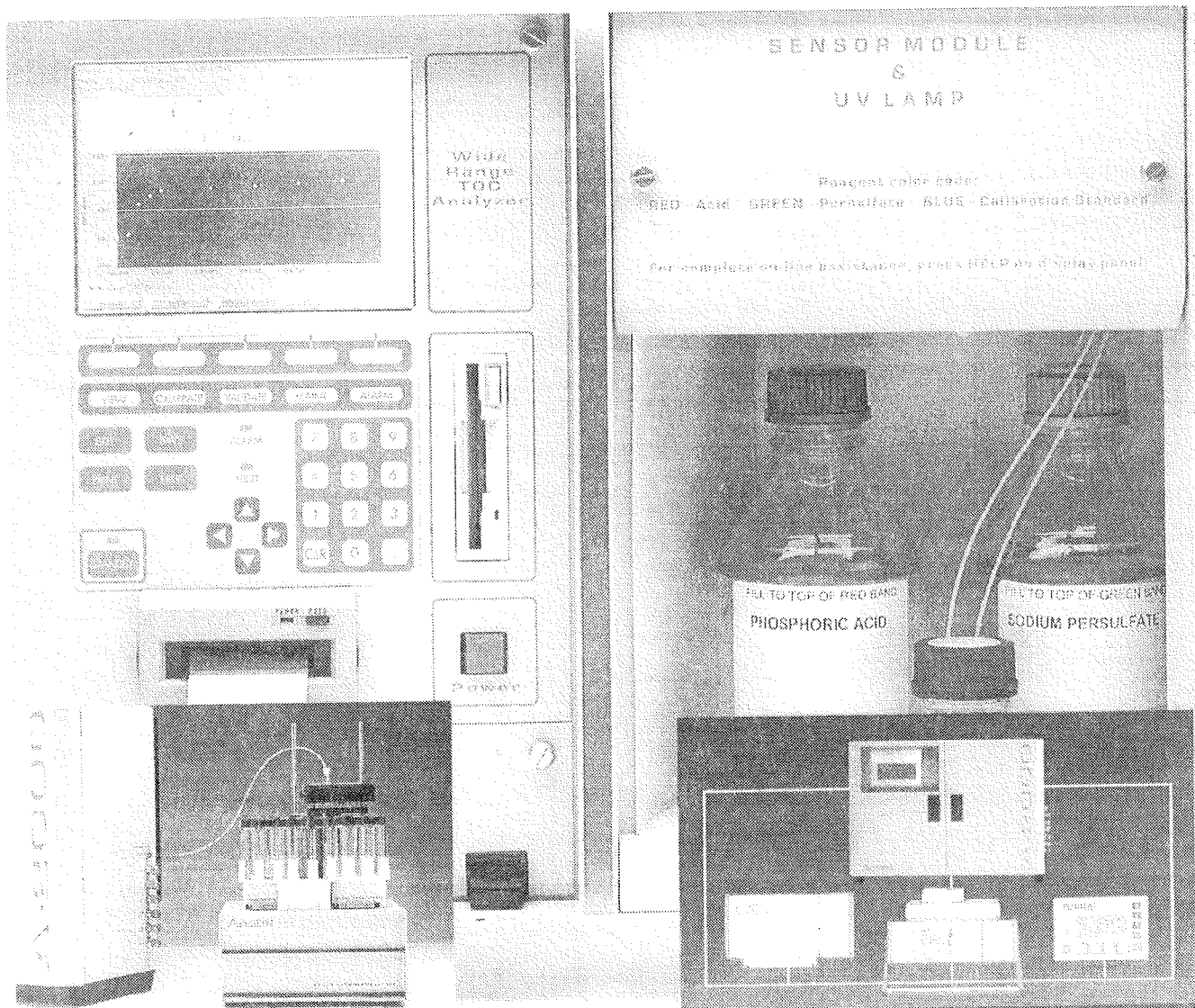


Figure 6: A-2000 system

Liquid/gas separator

The membrane in the liquid/gas separator chamber is actually round, silicone tubing, more than half a meter long, wrapped into a compact spiral measuring less than 2 inches in length. The water/reagent mixture permits only CO_2 to pass through the silicone wall as it flows through the tubing. This design maximizes the membrane surface area exposed to the sample mixture, so that the diffusion of CO_2 across the membrane is fast, efficient, and complete.

NDIR Detector

The NDIR detector consists of a single chamber (optical path) with an infrared light source at one end, and a filtered photodetector at the other end. The chamber is first filled with N_2 carrier gas to establish a baseline reading. Then the chamber is emptied, and filled with N_2 carrier gas mixed with the CO_2 sample. CO_2 in the optical path absorbs an amount of infra-red energy, at a specific wavelength, proportional to the amount of CO_2 present. Because the energy is absorbed, it never reaches the filtered photodetector, which outputs a signal proportional to the amount of CO_2 gas in the chamber. In this way, TOC is measured very accurately and precisely as the concentration of CO_2 produced by the sample oxidation.

Sample/Sparge Chamber

The sample/sparge chamber is actually a cylinder about 3" long and 1" in diameter, constructed of electro-polished stainless steel. The cylinder contains the acidified sample while N_2 carrier gas bubbles through

it. This bubbling action, known as "sparging", agitates the liquid sample, and frees the inorganic carbon (e.g. H_2CO_3 , CO_3^{2-} , HCO_3^-) from solution so it can escape into the atmosphere leaving a TIC free sample. The sample/sparge chamber is only used during the TOC fast operating mode.

Multi-Port Switching Valve

The electronically actuated multi-port switching valve is expected to provide reliable performance with continuous use for many years. The computer rotates the 8-port valve to control the flow of sample, acid, persulfate and calibration solution to the syringe pump, drain and other A-2000 components. Use of a multi port switching valve in combination with a syringe pump for mixing is part of the A-2000 sequential injection analysis (SIA) design.

Syringe pump

All initial mixing of liquid sample components takes place in the rugged digitally controlled syringe pump. Acid, persulfate and sample are precisely mixed according to modified, proven, sequential-injection-analysis (SIA) principles in this sturdy, long-lasting, computer controlled, glass syringe pump.

Reagents

All reagents used for operating the A-2000 wide range TOC analyzer can be easily purchased from any chemical supply house or can be ordered directly from Anatel for maximum convenience. 0.3 Molar phosphoric acid (H_3PO_4) is used to lower the sample pH and allow CO_2 and other dissolved purgeables to migrate

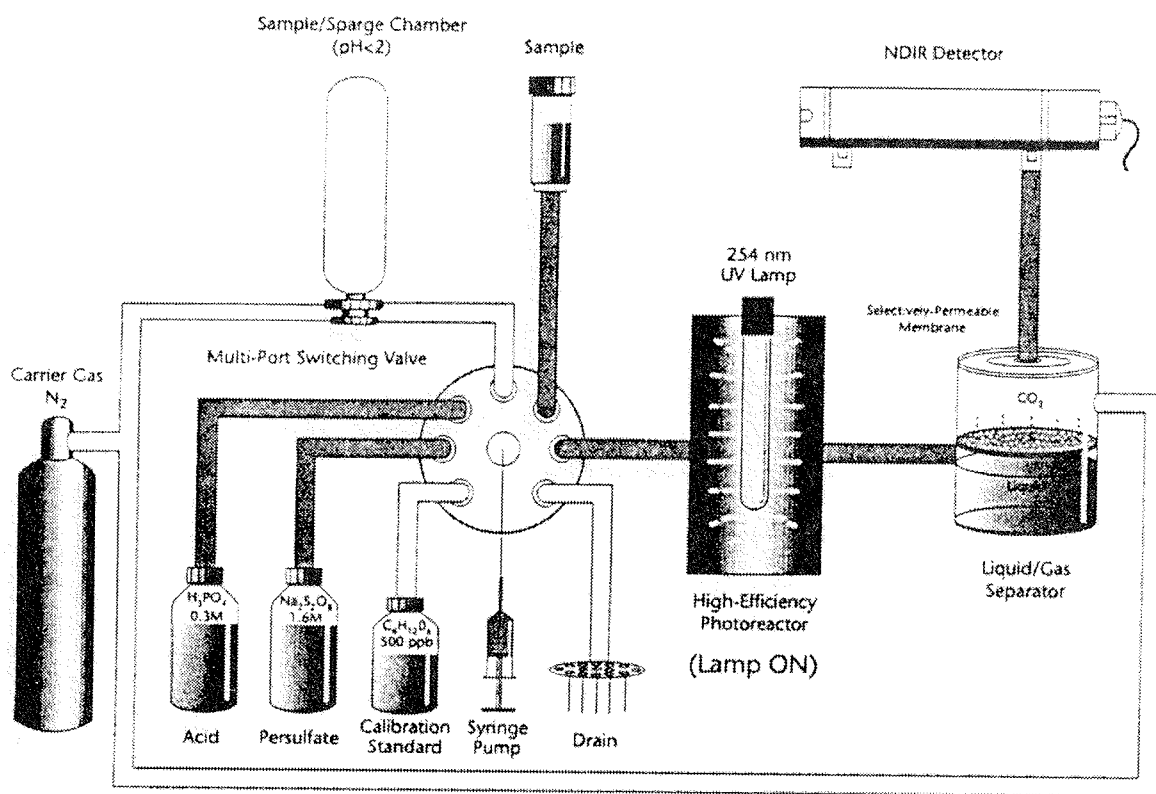


Figure 7: Operating schematic for measurement of TOC

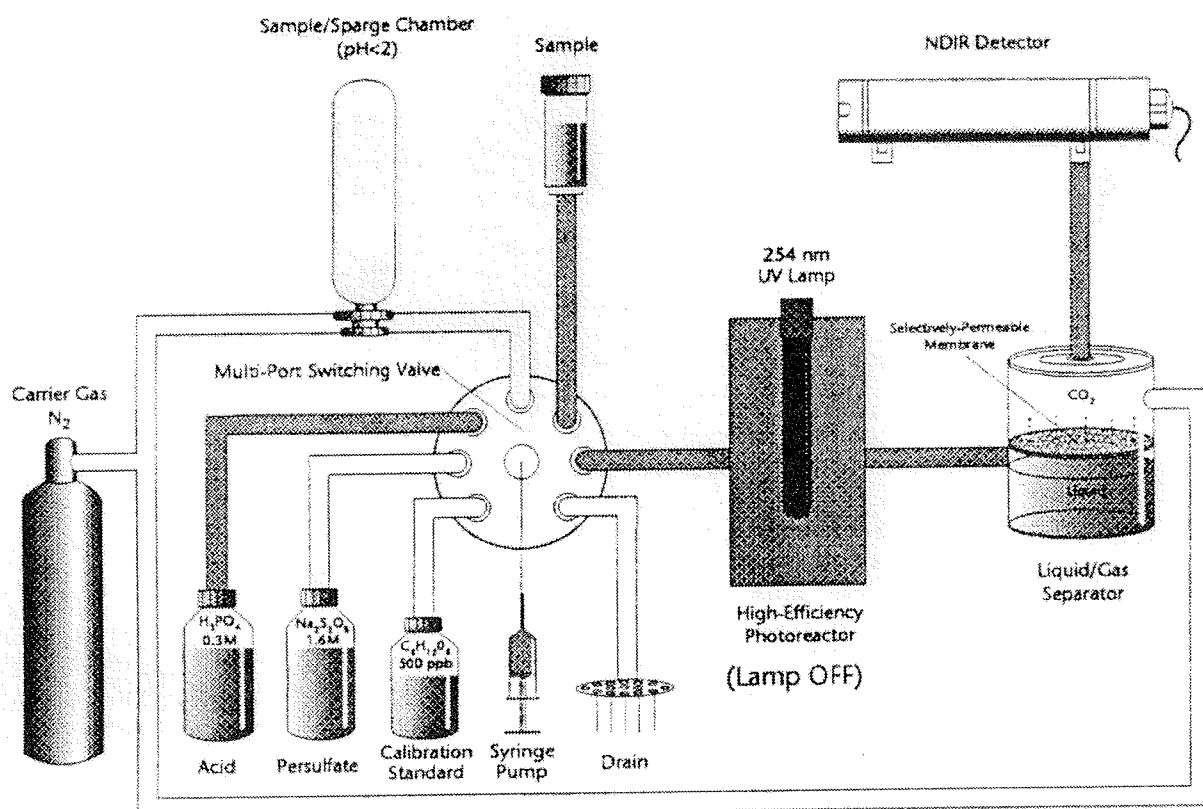


Figure 8: Operating schematic for measurement of TIC

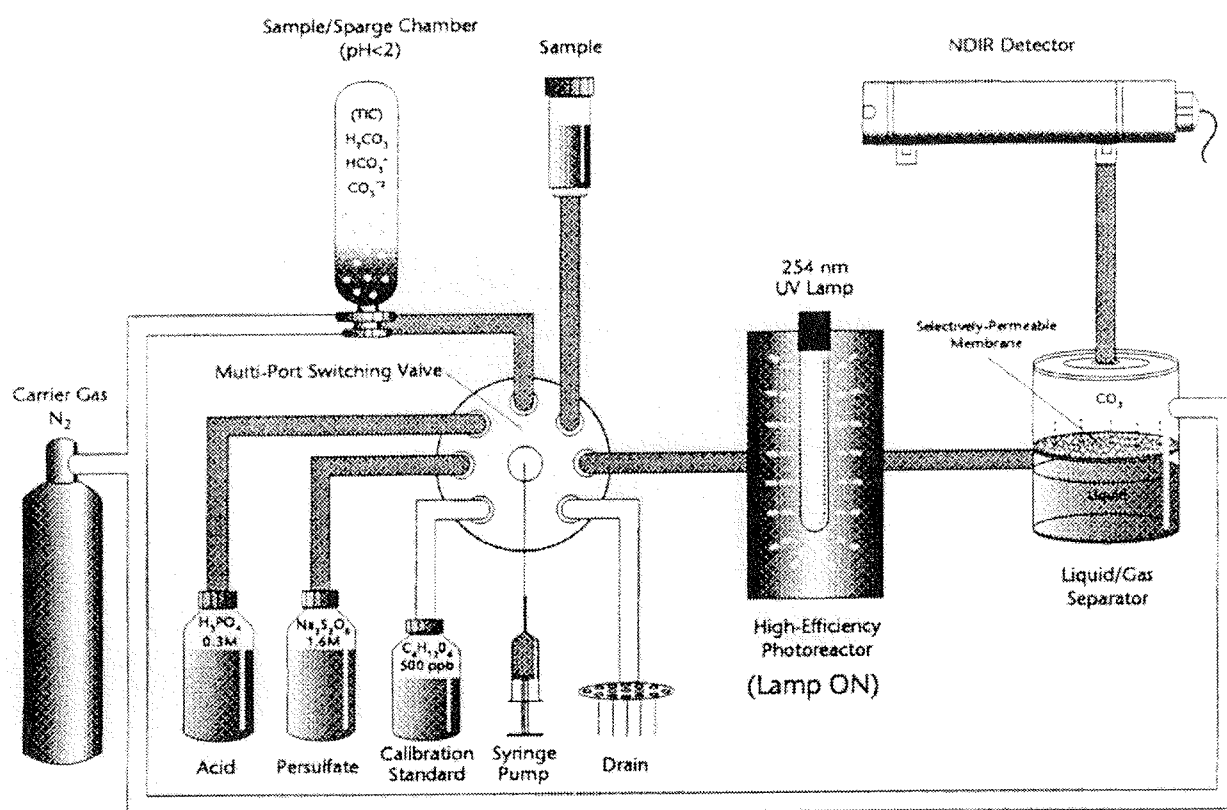


Figure 9: Operating schematic for measurement of TOC fast

out of solution. 1.6 Molar sodium peroxodisulfate ($\text{Na}_2\text{S}_2\text{O}_8$) is used, in conjunction with 254 nm UV energy, to oxidize the sample to CO_2 suitable for measurement by the NDIR detector. Anatel also provides 500 ppb sucrose ($\text{C}_6\text{H}_{12}\text{O}_6$) solution designed for pharmaceutical calibration of the instrument. Sucrose NF is the proposed calibration compound recently recommended to the United States Pharmacopeia (USP) for performing calibrations on TOC analyzers.

Carrier Gas

A-2000 carrier gas must be at least 99.98% pure nitrogen (N_2), pressurized to 4 bar, and capable of flowing at 250 ml/min. The carrier gas is used to sweep CO_2 and inorganic carbon (e.g. H_2CO_3 , CO_3^{2-} , HCO_3^-) to the NDIR cell for measurement. Additionally, carrier gas alone is used as a background measurement of NDIR performance.

4.2 Simplified A-2000 Operating Schematics

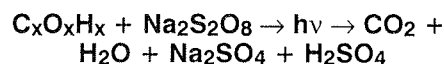
4.2.1 Total Carbon - TC

The A-2000 measures TC by oxidizing all of the oxidizable materials in the raw sample water, and measuring the amount of CO_2 produced by the oxidation.

1. Acid and sodium peroxodisulfate are added to the sample in the syringe pump. The persulfate oxidizes the sample while the acid allows CO_2 gas to escape from the acidified sample by lowering the sample pH.

2. The entire sample is transported directly to the high efficiency photoreactor, without sparging, and the sample molecules are oxidized to CO_2 and byproducts

according to the following equation:



254 nm UV energy accelerates and promotes the persulfate oxidation.

3. The resulting CO_2 is separated from the byproducts by diffusion through a selectively permeable membrane in the liquid/gas separator.

4. The CO_2 is transported to the NDIR detector within the N_2 carrier gas stream. The NDIR detector outputs a signal proportional to the concentration of CO_2 in the carrier gas stream.

4.2.2 Total Inorganic Carbon - TIC

To measure TIC, the A-2000 must separate the inorganic carbon (e.g. H_2CO_3 , CO_3^{2-} , HCO_3^-) from the sample solution, so that it can be measured.

1. The sample is adjusted to $\text{pH} < 2$ by adding phosphoric acid in the syringe pump which allows the TIC to dissociate as CO_2 .

2. The CO_2 is separated from the byproducts by diffusion through a selectively permeable membrane in the liquid/gas separator. The lamp stays off throughout the analysis to prevent any oxidation by the UV energy alone.

3. The CO_2 is transported to the NDIR detector within the N_2 carrier gas stream. The NDIR detector outputs a signal proportional to the concentration of CO_2 in the carrier gas stream.

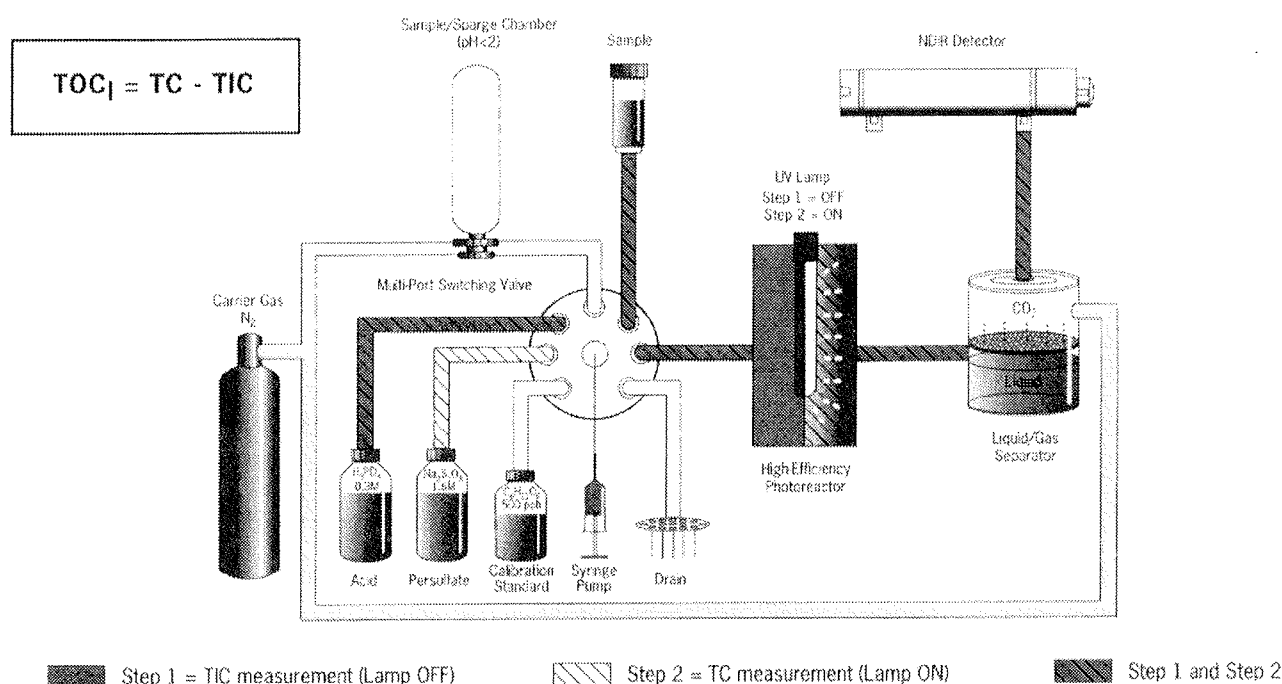
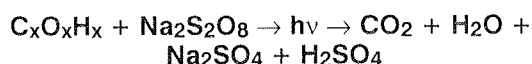


Figure 10: Operating schematic for measurement of TOC_I

4.2.3 Total Organic Carbon - TOC Fast

To measure TOC directly the A-2000 must first transport the sample to the sample/sparge chamber where the TIC (e.g. H_2CO_3 , CO_3^{2-} , HCO_3^-) is removed from the TOC by sparging.

1. The sample is adjusted to $\text{pH} < 2$ by adding phosphoric acid in the syringe pump.
2. The sparging process allows purified nitrogen gas to bubble through the sample mixture in the sample/sparge chamber. This bubbling action frees the inorganic carbon from solution so it can escape into atmosphere, leaving a TIC free sample.
3. The remaining TOC, still in liquid phase, is combined with sodium peroxodisulfate in the syringe pump and transported from the sample/sparge chamber to the high efficiency photoreactor where the molecules are oxidized to CO_2 gas by the addition of sodium persulfate and 254 nm UV energy:



3. The CO_2 is separated from the byproducts by diffusion through a selectively permeable membrane in the liquid/gas separator.
4. The CO_2 is transported to the NDIR detector within the N_2 carrier gas stream. The NDIR detector outputs a signal proportional to the concentration of CO_2 in the carrier gas stream.

4.2.4 Total Organic Carbon Determined Indirectly-TOCI

The removal of TIC when measuring TOC directly, can also result in the loss of low molecular weight TOC, or "purgeable organic carbon" (POC). When POC composes a significant portion of TOC, such as in the drinking water industry, it may be advantageous to measure TOC indirectly as the difference: $\text{TOC}_i = \text{TC} - \text{TIC}$. By measuring TOC indirectly, POC is included and measured as TOC.

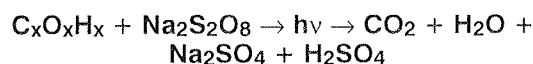
TOC_i is determined by separately measuring TC and TIC and calculating the mathematical difference.

Determination of TIC (UV lamp off):

1. An aliquot of the sample is adjusted to $\text{pH} < 2$ by adding phosphoric acid which allows the TIC to dissociate from the sample as CO_2 .
2. The sparging process allows purified nitrogen gas to bubble through the sample mixture in the sample/sparge chamber. This bubbling action frees the inorganic carbon from solution so it can escape into atmosphere, leaving a TIC free sample.
3. The CO_2 is separated from the byproducts by diffusion through a selectively permeable membrane in the liquid/gas separator.
4. The CO_2 is transported to the NDIR detector within the N_2 carrier gas stream. The NDIR detector outputs a signal proportional to the concentration of CO_2 in the carrier gas stream.

Determination of TC (UV lamp on):

1. Acid and sodium peroxodisulfate are added to a second aliquot of the sample in the syringe pump.
2. The second aliquote is transported directly to the high efficiency photoreactor without sparging, and the sample molecules are oxidized to CO_2 gas and byproducts according to the following equation:



254 nm UV energy serves as a catalyst and promotes the persulfate oxidation.

3. The CO_2 is separated from the byproducts by diffusion through a selectively permeable membrane in the liquid/gas separator.
4. The CO_2 is transported to the NDIR detector within the N_2 carrier gas stream. The NDIR detector outputs a signal proportional to the concentration of CO_2 in the carrier gas stream.

4.3 A-2000 performance specifications

Measured parameter:	TC, TIC
	TOC fast and $\text{TOC} = \text{TC} - \text{TIC}$
Measuring range:	TOC: 3 to 5000 ppb, 0.0 to 100.0 ppm, 0 to 2000 ppm
	TIC: 3 to 5000 ppb, 0.0 to 100.0 ppm, 0 to 2000 ppm
Precision:	TC/TOC/TIC $\pm 2\%$ in each range
Analysis time:	TIC: 1.5 min, TC: 3 min, TOC: 4 min
Sample introduction:	On-line
	Manual sipper tube
	Vial autosampler

Communications:	Network as many as 8 instruments
	Serial communication
	Four independent 0(4)-20 mA outputs
	Two user selectable alarm levels
	Relay outputs for alerts and alarms
User interface:	Full 8" backlit color LCD
	Convenient hard/soft key interaction
	Trend charts
	On-line help
Output devices:	Built-in internal printer
	Built-in floppy drive
	Optional external graphics printer
Calibration:	User selectable automatic or manual calibration
	Calibration from manual or autosampler vials
	Calibration from internal standard source
	Up to five calibration curves stored
	Automatic calibration reports
Validation:	Built in validation functions
	User selectable acceptance criteria
	Automatic validation reports
Gas requirements:	Nitrogen, 99.98% purity and better, 4 bar, 250 ml/min
Reagents:	Premeasured (or user prepared) 0.3M phosphoric acid and 1.6M sodium peroxodisulfate
	Easy reagent replacement
	Calibration standard - sucrose NH
	Reagent lifetime: 3 weeks
Dimensions:	H457mm x W635mm x D254mm
	Weight 32 kg
	90 to 240 VAC \pm 10%, 50/60Hz, 650VA
Optional autosampler:	H457mm x W286mm x D267mm
	Weight 10 kg
	27 vials (40 ml EPA type)
	90/120 VAC, 220/240VAC, 50/60Hz, 200VAmx

5.0 LITERATURE

- /1/ K.G. Malle, "Cleaning Up the River Rhine", Scientific American, January 1996
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- /3/ F. Blades, C. Frith, "New Analytical Technique for On-Line Detection of Trace Organics in Ultrapure Water", Seventh International Symposium of Contamination Control, Paris (18. September 1984)
- /4/ M. Retzik, P. Melanson, "The Design, Performance, And Validation Of An On-Stream Total Organic Carbon Analysis System For Monitoring Ultra Pure Water", International Conference, Instrument Society of America (September 1993)

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