Evaluation of 3 Commercially Available, On-line TOC Analyzers for Monitoring Recycled Water in Semiconductor Processing

Robert P. Donovan and Dennis Morrison
Sandia National Laboratories
Albuquerque, NM 87185

John DeGenova
SEMATECH
Austin, TX 78741

Introduction

Rapid detection of excursions in the concentration of organic contaminants in water that is being recycled is crucial to the more widespread acceptance of rinse water recycling as a method of reducing water usage in semiconductor manufacturing. In 1995 SEMATECH'S S116 PTAB (Project Technical Advisory Board) arbitrarily targeted a response time of 30 s as the goal for the on-line detection of TOC (Total Oxidizable Carbon) in water – a goal thought to simplify the design of water recycling systems (less volume required for water storage in the recycle loop) and lead to more widespread adoption of recycling of spent rinse waters by the US semiconductor industry. A subsequent evaluation of the TOC analyzers commercially available in early 1996 demonstrated that the fastest response times were on the order of three minutes [Ref. 1].

This paper updates the 1996 evaluation of commercially available TOC analyzers by assessing modified versions of two of the previously evaluated analyzers and also a new analyzer that became commercially available in 1997.

Background

Virtually all on-line analyzers of TOC in water use UV radiation or a combination of chemical oxidation and UV to convert the organic carbon in the sample to CO₂. The CO₂ creates electrically conductive ions in the water sample which increase the sample conductivity so that measuring the increase in water sample conductivity following the oxidation step becomes one method of measuring the nonconductive organic contaminant from which the newly created CO₂ originated. Non-dispersive infrared (NDIR) absorption is a second, commonly used technique for measuring the concentration of this CO₂. The NDIR measurement, however, requires that the CO₂ be separated from the water matrix.

When the increase in conductivity is measured directly in the water sample, the presence of other conductive species that may be present in the sample raises the background conductivity of the sample, making small increases in sample conductivity more difficult to detect accurately. The formation of conductive species in the UV reactor other than CO₂ from oxidizable carbon can also confound a conductivity-based measurement of TOC made directly in the water sample. In an indirect measurement, a detection chamber
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
DISCLAIMER

Portions of this document may be illegible electronic image products. Images are produced from the best available original document.
is isolated from the water sample, for example by a semipermeable membrane, but is coupled to its properties by the transport of CO₂ through that membrane or other isolating media. In the detection chamber, the CO₂ concentration can be measured by either the conductivity changes induced in an ultrapure water loop or by NDIR absorption in a gas medium. This transport step through the membrane or other isolating media, while minimizing interferences, lengthens response time.

The newly available TOC analyzer taking part in the test series is a direct measuring analyzer; the other two are indirect.

Metrics

Response time is the primary analyzer property of interest. Accuracy in the measurement of concentration is less important. Trading measurement accuracy for speed of response to TOC identifies a distinct priority for TOC analyzers that are tailored for the water recycle market in semiconductor manufacturing. Early warning that a threshold of TOC concentration has been exceeded is more important than accurately knowing by how much. An early alert allows timely diversion of the suspect recycled water before it introduces problems into the production line. Troubleshooting can begin after the production line has been protected.

Oxidation of Organic Carbon by UV Radiation

The oxidation of organic species in water is usually a series of chemical reactions between the organic compound and the hydroxyl radical, OH*, represented as follows:

\[ \text{CH} + \text{OH}^* = \ldots + \text{OH}^* = \ldots + \text{OH}^* = \text{CO}_2 + \text{H}_2\text{O} \quad (1) \]

Ultra violet radiation is a common method for creating hydroxyl radicals in water. Persulfate compounds are commonly used in the chemical oxidation reaction.

The rate at which this reaction proceeds varies with the particular organic species, as does the composition of the intermediate species. The conductivity of the intermediate species also varies so that water conductivity as a function of time of UV radiation often looks like the P3 Type oxidation curve as shown in Figure 1. The peak in conductivity reflects the fact that the intermediate organic species are often more conductive than the end product CO₂ which reaches an equilibrium in water as described by Eq. 1. This species dependence of oxidation rate and contribution to conductivity must be accounted for in the algorithms relating conductivity changes to TOC.
The relationship between conductivity and time is called the "oxidation curve." Three forms of oxidation curve are reported: Profile Type 1 ("P1"), Type 2 ("P2") and Type 3 ("P3").

Conductivity is always increasing until oxidation is complete in a P1 sample. This indicates that few intermediate organic acids, which have higher conductivity than the equivalent CO₂, are formed. A P3 sample contains significant amounts of these acids. Consequently, conductivity peaks then decreases as completion nears. P2 samples occur at low TOC levels and are very similar to a P1, or minor P3, sample in which the organic "background" of the measurement cell must be adjusted.

Abrupt changes in the Profile Type can indicate a change in water chemistry. For example, a change from a P2 to a P3 Profile Type at a TOC level of 10 ppb, indicates a contamination shift towards more complex compounds. This comparison is also valid between water treatment systems when TOC levels are similar. Note that changing to the "Fast" Analyze Rate may change the Profile Type. The "Normal" Analyze Rate is recommended for applications where the Profile Type is of interest.

Simple organics, such as methanol, report P1 up to relatively high levels (in excess of 500 ppb). More complex organics tend to oxidize as a P3 Type at all but the lowest levels (less than 25 ppb). In this instance, complex indicates either very large organics with a high molecular weight or organics that contain some element which resists oxidation. As TOC levels vary, the location of this transition shifts but the accuracy of the measurement is maintained. Neither the Profile Type nor the analysis conditions cause any variations in TOC readings.

Figure 1 Types of Oxidation Curves (from Anatel A-1000 manual)
Accounting for Fully Oxidized Carbon (Inorganic Carbon) Present in the Sample

Only the indirect measuring TOC analyzers account for the inorganic carbon also present in a sample. Fully oxidized, inorganic carbon in a water sample exists as CO₂, carbonate or bicarbonate ions. It is removed by acidifying the sample, driving the equilibrium in the following equation to the right

\[ 2H^+ + CO_3^{2-} \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_2 + H_2O \]  

(2)

At pH < 3 - 4 virtually all the inorganic carbon is present as CO₂ as shown in Fig. 2. Indirect measuring TOC analyzers then either measure the total inorganic carbon (TIC) as part of the analysis or eliminate it by sparging or otherwise degasifying the sample prior to the UV oxidation step.

Direct measuring TOC analyzers ignore the presence of inorganic carbon which can confound the measurement of TOC and limit the useful operating range of the analyzer—just like any other conductive species in the water that raises the background conductivity.

![Figure 2. INFLUENCE of pH on INORGANIC CARBON SPECIES](from Jolly, C. D. and E. L. Jeffers, "Ultrapure Water Total Organic Carbon Analyzer—Advanced Component Development", SAE Paper 911436, SP-874, SAE, 400 Commonwealth Drive, Warrendale, PA 15096-0001)
Test Setup

Figure 3 is a schematic of the test array set up for the evaluation. Five TOC analyzers (the three test analyzers plus two referee analyzers) were run in parallel from a common source of ultra pure water (UPW) which could be spiked with known organic analytes and other challenge solutions at known, constant concentrations. The analyzer designations were A, B, C, Ref. 1 and Ref. 2. Analyzers A and B were upgraded/modified versions of the analyzers similarly labeled in the 1996 evaluation; C was the newly announced analyzer.

A third reference analyzer joined the evaluation for a brief period. Neither this analyzer nor referee analyzers 1 & 2 were evaluated as candidates for the recycling application, since all these analyzers have long response times and two of them operate in a batch mode rather than a continuous mode – these two analyzers draw a sample from the monitored water stream and then isolate that sample and the TOC analyzer from the monitored water stream during the period of the analysis. These analyzers are in effect off-line during the time period in which the analysis is being conducted, leaving the
monitored water stream unmonitored for the majority of the time (the sampling period is shorter than the analysis time). This operating mode is thus less suitable for water recycling which demands continuous monitoring – sampling of all water being recycled should be carried out all the time.

The test array was set up in the basement of Sandia’s Microelectronics Development Laboratory (MDL) beneath the fab but with easy access to the UPW lines supplying the fab. This UPW was the primary matrix into which various challenge analytes were injected. UPW for the test series was routed through a coarse particle filter upstream of a magnetic flow meter. It then entered an injection fixture, which allowed a motor driven syringe to inject an analyte through a septum at the rate required to add the concentration of analyte needed to achieve a predetermined oxidizable carbon concentration. To obtain a desired concentration of carbon by weight in the water reaching each analyzer, the following relationship was used:

\[ c = \frac{A L M}{F} = \frac{F^* M}{F} \]  

where

- \( c \) = Oxidizable carbon concentration by weight in the stream reaching each analyzer
- \( A \) = Area of the syringe plunger
- \( L \) = Speed at which the motor driven plunger advances
- \( M \) = Oxidizable carbon concentration by weight in the syringe
- \( F \) = Volume flow rate of UPW as read by the magnetic flow meter
- \( F^* = A L \) = volume flow rate of solution injected by the syringe

For the syringe used in the test series, \( A = 5 \text{ cm}^2 \). \( L \) could be varied from \( 10^{-4} \) to \( 9 \times 10^{-3} \) cm/s. A convenient starting value of \( L \) was \( 5 \times 10^{-4} \) cm/s which permitted the injection of a constant concentration of oxidizable carbon for 3 – 4 hrs. In the actual test runs, feed speeds were often changed during a challenge in order to evaluate analyzer performance as a function of the concentration of oxidizable carbon in the challenge water stream. With \( L = 5 \times 10^{-4} \) cm/s and \( F = 1050 \text{ cm}^3/\text{min} \) (a typical value when all five analyzers were in the measurement system) the dilution ratio of the injection system, \( F^*/F \), equals 7000.

Two mixers downstream of the injector promoted a uniform distribution of the analyte injected into the stream. The challenge stream then passed through a conductivity cell and a pH cell prior to tee junctions that distributed the stream to each of the analyzers in parallel. All feed lines were \( \frac{1}{4} \) inch Teflon. The length of each line from the tee to the inlet of each analyzer was fixed at 3 feet.

**Procedure**

After the initial plumbing of the test setup, UPW flowed continuously through the induction system and all analyzers, 24 hours a day, seven days a week. When the syringe was not inserted through the septum in the injector, an orifice in the septum was partially
opened so that UPW could flow out of the injection port. This procedure minimized the
growth of bacteria in what otherwise would be a small dead space between the septum
and the main water flow through the injector.

To initiate a challenge run composed of a single organic analyte, the first step was to
calculate the concentration needed for the syringe charge. If the dilution factor, \( \frac{F^*}{F} \), is
taken to be 7000, achieving a challenge concentration of 100 ppb at the analyzers
requires a syringe charge of 700 ppm. This concentration was a typical value used to
prepare syringe charges, although for some low solubility analytes, such as p-xylene, the
analyte concentration in the syringe was deliberately lowered to 100 ppm.

Typically, the volume of UPW in the syringe was 50 cm\(^3\) so the desired weight of
oxidizable carbon in the syringe became:

\[
M = 700 \times 10^{-6} \text{ g} \]

\[
= \frac{\text{wt. [g] of oxidizable carbon}}{50 \text{ g}} \]

or

\[ \text{wt. of oxidizable carbon (g) = 35000 x 10^{-6} = 35 \times 10^{-3} } \] \hspace{1cm} (4)

The weight of an analyte molecule needed to provide this weight of oxidizable carbon is:

\[ \text{wt. of analyte (mg) = } \left[ \frac{\text{MW}}{\text{#C}(12.01)} \right] [35] = 2.91 \frac{\text{MW}}{\text{#C}} \] \hspace{1cm} (5)

where

\[ \text{MW} = \text{the molecular weight of the analyte molecule} \]

\[ \text{#C} = \text{the number of carbon atoms in each analyte molecule} \]

When the source of the oxidizable carbon is a liquid, eq. (5) becomes:

\[ \text{Vol. of liquid analyte (\mu l) = } 2.91 \frac{\text{MW}}{(\#C)(\rho)} \] \hspace{1cm} (6)

where

\[ \rho = \text{the density of the analyte (mg/\mu l)} \]

Equations (5) and (6) specify the quantity of analyte required in 50 ml of UPW in order
to produce a solution consisting of 700 ppm oxidizable carbon. When this solution is
injected at a flow rate of 0.15 cm\(^3\)/min into a UPW flow of 1050 cm\(^3\)/min, the resulting
concentration of oxidizable carbon in the mixture is 100 ppb.

As previously shown in equation (3), different concentrations of oxidizable carbon, \( c \), can
be delivered to the analyzers under test by changing the concentration of the analyte in
the syringe, \( M \); by changing the UPW flow rate, \( F \); or by changing the speed of the motor
driven syringe drive, \( L \), and hence the syringe feed flow rate, \( F^* \). The most common
operating mode and the simplest was to hold \( M \) and \( F \) constant and vary \( c \) by varying \( F^* \).
Indeed the simplicity of this step and the accuracy of the stepping motor over two orders of magnitude in drive speed, L, are major advantages of this test configuration.

Table 1 lists the analytes selected to challenge the TOC analyzers and the values of MW, #C and p used in eqns. (5) and (6) to calculate the quantities needed in the preparation of known concentrations of oxidizable carbon for each analyte except the two proprietary surfactants for which this information was not available. Most of the organic analytes came from a list previously prepared by the SEMATECH S116 PTAB; other analytes were included to extend the range of variables, such as resistivity and pH, thought to be representative of the spent rinse waters that are amenable to recycling.

For most preparations from a liquid source, an Eppendorfpipette was used to inject the volume of analyte calculated from eq. (6) directly into a syringe filled with 50 ml of UPW. This procedure generally consisted of injections of less than 100 μl of analyte, a capability well within the range of an Eppendorfpipette. Accuracy, however, was not as high as when a stock solution was made up in larger volumes (100 – 500 ml) external to the syringe and transferred into the syringe for injection into the test setup. All challenge solutions prepared from solid analytes used the external stock solution technique. An electronic micro balance (Mettler Model #AE240) was used to accurately weigh a given mass of solid analyte which was then transferred to either a graduated cylinder or a volumetric flask. The quantity of water needed to maintain the proportion calculated in eq. (5) for 50 ml of UPW was then added. Once well mixed this solution was poured directly into the syringe for injection.

The primary metric of the evaluation was the relative response times of the analyzers under test. To measure this parameter the TOC outputs of the three continuous, on-line analyzers were logged into a laptop computer using customized software. Analyzers A & B were interrogated every 4 s which approximates the data output rate of Analyzer B. (Analyzer A outputs every second but logging every 4 s provided adequate resolution.) The RS232 output from Analyzer C updates only every minute. A Metrosonics data logger was added to average its TOC readings over every 2 s. The data for these averages were read from the recorder output terminal of the analyzer. The Metrosonics record was then combined with the RS232 logs to generate 4 curves of TOC vs time for the three analyzers, two of the curves being data from Analyzer C.

Response times were measured in two ways:
1. From the time the syringe motor was turned on (or off) to initiate (or stop) the challenge spike to the time that the TOC value reached 10% of its final value (t₁₀);
2. From the time the syringe motor was turned on (or off) to initiate (or stop) the challenge spike to the time that the TOC value reached 90% of its final value (t₉₀).

Both rise times (t₁₀; t₉₀) and fall times (t₁₀; t₉₀) were measured during various challenge tests. Transit time in the lines connecting the injector to each analyzer is part of these measured response times. These transit times depend upon the flow rate to each analyzer, including the bypass flow features each analyzer incorporates to minimize the sample
Table 1. Challenge Analytes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>MW</th>
<th>#C</th>
<th>ρ (mg/μl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>C₃H₆O</td>
<td>58</td>
<td>3</td>
<td>0.79</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>C₆H₁₂</td>
<td>84</td>
<td>6</td>
<td>0.78</td>
</tr>
<tr>
<td>IPA</td>
<td>(CH₃)₂CHOH</td>
<td>60</td>
<td>3</td>
<td>0.804</td>
</tr>
<tr>
<td>Methanol</td>
<td>CH₃OH</td>
<td>32</td>
<td>1</td>
<td>0.791</td>
</tr>
<tr>
<td>MEK</td>
<td>CH₃COCH₂CH₃</td>
<td>72</td>
<td>4</td>
<td>0.805</td>
</tr>
<tr>
<td>NMP</td>
<td>C₆H₅O</td>
<td>99</td>
<td>5</td>
<td>1.03</td>
</tr>
<tr>
<td>Phenol</td>
<td>C₆H₅OH</td>
<td>94</td>
<td>6</td>
<td>1.07</td>
</tr>
<tr>
<td>Amyl Acetate</td>
<td>C₇H₁₄O₂</td>
<td>130</td>
<td>7</td>
<td>0.876</td>
</tr>
<tr>
<td>Butyl Acetate</td>
<td>C₆H₁₂O₂</td>
<td>116</td>
<td>6</td>
<td>0.88</td>
</tr>
<tr>
<td>p-xylene</td>
<td>C₈H₁₀</td>
<td>106</td>
<td>8</td>
<td>0.866</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>C₂H₆O₂</td>
<td>62</td>
<td>2</td>
<td>1.109</td>
</tr>
<tr>
<td>TMAH</td>
<td>(CH₃)₄NOH</td>
<td>91</td>
<td>4</td>
<td>1.0</td>
</tr>
<tr>
<td>FC-93 Perfluoroalkyl sulfonate</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>OHS Alkyl phenoxy polyglycidol</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>Acetic acid</td>
<td>CH₃CO₂H</td>
<td>60</td>
<td>2</td>
<td>1.049</td>
</tr>
<tr>
<td>Chloroform</td>
<td>CHCl₃</td>
<td>119</td>
<td>1</td>
<td>1.484</td>
</tr>
<tr>
<td>KHP</td>
<td>KH₂C₈O₄</td>
<td>204</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Sucrose</td>
<td>C₁₂H₂₂O₁₁</td>
<td>342</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>Sodium Carbonate</td>
<td>Na₂CO₃</td>
<td>106</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Potassium chloride</td>
<td>KCl</td>
<td>74.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
transit time. The flow between the injector and the distribution tees is common to all analyzers. Challenge solution residence time in the housings for the pH and resistivity cells dominated the transit time between the injection point and the analyzers and was estimated to be 22 – 24 s. The manufacturer-specified sample flows through the actual measuring loops of each analyzer are 7.5 ml/min for Analyzer A; 1.0 ml/min for Analyzer B; and either 75 ml/min or 20 ml/min for Analyzer C.

The relatively remote location of the injection port to each analyzer plus the turbulent flow deliberately introduced by the mixers to promote a homogeneous water sample distort the form of the challenge spike from that of a sharp step function to a more diffuse shape. Thus, the measured response shapes reflect properties of the test configuration as well as analyzer properties. However, the relative response times remain clear.

A second metric of importance was accuracy of measurement. Trading accuracy for speed has been the recommended tactic for achieving rapid detection of TOC excursions but responses must be unambiguous in interpretation. Percent recovery was calculated as the ratio of the measured concentration/the concentration of the challenge solution prepared as described earlier.

Reliability and ease of use are also properties of interest but can be commented on only cursorily, being based on a time period short with respect to an average expected life of such analyzers.

**Results**

The data plots presented can consist of as many as five different colored curves. In addition to the 4 TOC plots, the figures show a marker along the top of the plot. This marker roughly corresponds to the initiation of the analyte injection and its conclusion. It was manually actuated in coordination with the manual flipping of the switch that started or stopped the syringe drive motor.

**Analyzer A**

Analyzer A is an updated version of that previously evaluated in the 1996 test series. This new version incorporates a number of improvements that make the unit more user friendly and versatile. The most important improvement, however, has been its superior reliability of operation. This version was in continuous operation for 5 months during which period it took itself off line just once and was immediately returned to service without further diagnostics. Sliding the front panel of the analyzer forward to access the components for corrective action or adjustments, a task repeatedly performed with the earlier model, was not necessary even once with this newer version. Even the acidifier bottle is now external to the component chamber and can be refilled without opening the instrument case. When operating in its turbo mode, the mode most appropriate for
recycle operations but also the mode requiring the highest acid flows, the acid bottle required refilling every 3 weeks.

Another significant change is the availability of a total carbon (TC) measuring mode in addition to the conventional TOC mode. In the earlier evaluation, several of the volatile challenge analytes were lost or depleted by the TIC-removal GLS (gas liquid separator), giving the analyzer a low percent recovery for that analyte. The present version of Analyzer A includes the option to select the measurement of TC rather than TOC. With the TC measurement selection, the TIC GLS is bypassed and the water stream enters the UV reactor without having the TIC removed. This configuration eliminates the loss of volatile TOC in the TIC removal step but also means that the distinction between TC and TOC is lost — the output is no longer a measure of just TOC.

The analyzer can be programmed to switch between the TC and TOC measurement modes but such a switch requires at least three minutes of off-line time in which the water stream within the analyzer is being rerouted and is establishing a new steady state in the IR detector. During this off-line period, no information about the water stream being monitored is available. Assuming even this brief off-line period is unacceptable, the user is then forced to choose between losing high recovery of volatile organic contaminants such as chloroform (TOC mode) or having inorganic contaminants included in the reported concentration of carbon (TC mode). TOC and TC cannot be measured simultaneously. Most measurements conducted during this evaluation were made in the TOC mode but with several analytes, the mode was switched to TC periodically during the challenge.

Physically, Analyzer A remains a bulky unit, more the size of a small refrigerator than the briefcase size of the conductivity-based analyzers. It is an indirect analyzer using membranes to separate CO₂ from the water sample. It measures the concentration of CO₂ by an NDIR method, making the TOC measurement insensitive to other conductive species that may be in the sampled water or formed in the UV reactor. On the other hand CO₂ in the IR cell that originates from sources other than the water sample can raise the background level of CO₂ in the IR cell and contribute errors to the reported TOC. Historically, NDIR-based TOC analyzers have had poorer detection limits than conductivity-based TOC analyzers. The manual lists 20 ppb as its detection limit. No attempt was made to determine a limit of detection for Analyzer A, or any of the analyzers evaluated, since single digit ppb concentrations are not in the range of primary interest in recycling.

Response Time

Typical values of response times for Analyzer A were:

\[
\begin{align*}
  t_{10} & \quad 160 - 230 \text{ s} \\
  t_{90} & \quad 210 - 300 \text{ s}
\end{align*}
\]
t_{f10} \quad 165 \text{ s}

t_{f90} \quad 200 \text{ s}

Some of the times above are slightly faster than those reported in the 1996 evaluation, even though no correction was made to account for the line delays between the injection port and the analyzer entry. Analyzer A now includes a bypass valve that allows the volume flow rate in the feed line delivering the water sample to exceed the volume flow rate of the sample water in the analytical section by a factor of 15 – 20. The earlier version of Analyzer A did not have this feature.

Percent recovery

Percent recovery for most of the challenge analytes fell within the target range of 100% +/- 30% when operating in the TOC mode. However, some analytes were underestimated: p-xylene, cyclohexane, chloroform and, to a lesser degree, butyl acetate and amyl acetate. In the TC mode, all of these analytes were satisfactorily detected. Figure 4 illustrates Analyzer A’s response to chloroform in both its TC and TOC modes. (Similar data for Analyzer B, to be discussed next, also appear.) The initial readings of Analyzer A, challenged with nominally 100 ppb of CHCl₃, are about 80 ppb in the TC mode. When switched to TOC mode, the readings with this same analyte challenge drop to 15 – 20 ppb. The difference between the two modes, while measurable, is much less for butyl acetate as illustrated in Fig 5. In both modes, the recovery efficiency for butyl acetate is within 100% +/- 30%. Analyzer A’s response to amyl acetate is similar to that of butyl acetate.

Summary, Analyzer A

Analyzer A performed much better in this test series than in the previous evaluation conducted in 1996. Historically, on-line TOC analyzers using NDIR detectors have not succeeded in penetrating the semiconductor industry to any significant extent. This analyzer in this application makes sense if its size and weight can be accommodated. Its primary shortcoming in these tests was the loss of certain volatile organic analytes in the TIC GLS. The alternative of operating Analyzer A continuously in its TC measurement mode, while minimizing the loss of volatile organics and actually slightly speeding up the analyzer response time, is unattractive for recycle operations where most of the spent rinse waters being recycled are likely to be CO₂ saturated. Without TIC removal, the TIC background contribution to TC is thus likely to be in excess of several hundred ppb, masking the TOC concentrations and complicating their measurement. A more appropriate strategy would seem to be continuous monitoring in the TOC measurement mode, assuming that any volatile organics lost in the TIC GLS would likely be easily removed by conventional degasification hardware already in widespread use in semiconductor UPW plants.
Figure 4. Improved Recovery of Chloroform in the TC Mode of Analyzer A

100 ppb Chloroform (pH: 7.0; rho: 17.8 Mohm-cm)
Analyzer A: TC mode initially; to TOC mode at 12:55
Analyzer B: ICR in-line initially; to bypass at 12:46; to in-line at 13:05

Figure 5. Recovery of Butyl Acetate by Analyzers A and B with and without Removal of Inorganic Carbon

100 ppb butyl acetate (pH: 8.0; rho: 17.8 Mohm-cm)
Analyzer A: TOC mode initially; TC at 11:46; TOC at 12:24
Analyzer B: ICR on-line initially; to bypass at 11:46; to on-line at 12:24
Analyzer B

Analyzer B measures water sample TOC indirectly, using a semipermeable membrane to separate the sample water from a reference source of UPW and relying on CO₂ transport across the membrane to equalize CO₂ concentrations in the water on each side of the membrane. The increase in the conductivity of the UPW brought about by the CO₂ added to the UPW is a measure of the TOC in the water sample. This analyzer was operated with an inorganic carbon removal (ICR) unit on its water inlet, the configuration deemed most appropriate for use in water recycle service.

Response time.
Typical response times of Analyzer B were as follows:

\[
\begin{array}{c|c}
 t_{10} & 210 - 250 \text{ s} \\
 t_{90} & 300 - 370 \\
 t_{100} & 190 \\
 t_{90} & 260 \\
\end{array}
\]

Percent Recovery
Analyzer B with the upstream ICR module was not calibrated on site but had been calibrated by the manufacturer immediately prior to shipping. Nonetheless, it invariably reported TOC concentrations somewhat lower than the nominal challenge concentrations.

The high concentrations of TIC expected in spent rinse waters make the use of an ICR almost mandatory in recycle applications. Otherwise, the TOC measurement is deduced from the difference between two large numbers – the TC and the TIC, both of which reflect the presence of the large concentration of TIC. Under these conditions the precision of the TOC measurement degrades significantly, often, for example with low true values of TOC and high TIC, displaying negative concentrations! Thus, except where noted in a few instances, all data collected with Analyzer B was from a configuration that included the upstream ICR.

The ICR module uses a membrane separator with low pressure ambient air on the gas side to remove the CO₂ from the sample water after sample acidification. All inorganic carbon of the sample water is assumed to be removed as CO₂ by this step. Unfortunately, some volatile organic species can also be lost in this step. In Fig. 4, Analyzer B with an upstream ICR in line exhibited low recovery of 100 ppb chloroform. Bypassing the ICR greatly improved recovery efficiency. Other challenge analytes partially lost in the ICR were p-xylene, butyl acetate (Fig. 5) and amyl acetate. Recovery of these analytes was also greatly improved when bypassing the ICR.

As noted in the introduction, the addition of upstream stages to remove sample TIC increases the response time of the analyzer. Bypassing the upstream ICR reduced the
response times of Analyzer B by about 30 s. Figures 6 - 8 illustrate the impact of the inorganic removal stages on response time. Each of these figures plots responses to a challenge of 400 ppb KHP. Figure 6 shows the response characteristics with the analyzers in the normal configuration; that is, the ICR unit is in-line upstream of the Analyzer B; Analyzer A is operating in its TOC mode. The \( t_{10} \) of Analyzer A is slightly faster than that of Analyzer B. In Fig 7, the challenge is repeated with Analyzer B’s ICR in bypass. Now the \( t_{10} \) response times of the two units are essentially identical. For the final plot of this series (Fig. 8), Analyzer A has been switched to its TC mode with the ICR of Analyzer B still in bypass. Analyzer A again displays a slightly faster rise time, although perhaps not as pronounced as with the typical configuration (Fig. 6).

**Summary, Analyzer B**

Analyzer B with an upstream ICR exhibited response times of \( t_{10} \sim 210 - 250 \) s and \( t_{90} \sim 300 - 370 \) s in the test configuration of this evaluation. The analyzer was adequately accurate over the range of concentrations tested. It accurately measured TOC in a matrix of equivalent TIC. It did not respond to challenges consisting of just inorganic carbon or those consisting only of noncarbon conductive species. While several volatile organic species were poorly recovered with the ICR in-line, operating with an on-line, upstream ICR is the configuration deemed most appropriate for recycle operations. The poorly detected analytes lost in the ICR are those that would be easily removed by conventional degasification modules. While switching from ICR in-line to ICR in bypass is simple and can be accomplished without interrupting the data stream or going off-line, this switch is not advisable with recycle water samples that have high TIC concentrations.

![Graph](image_url)

**Figure 6. Response Times with the ICR in-line (Analyzer B); Analyzer A, TOC Mode**
Figure 7. Response Times: ICR in Bypass (Analyzer B); Analyzer A in TOC Mode

Figure 8. Response Times with ICR in Bypass (Analyzer B); Analyzer A in TC Mode
Analyzer C

As noted earlier, two data sources were used to plot TOC measurements from Analyzer C. The data collected from the RS232 port are plotted as “C (rs232)” and the data from the recorder terminals are plotted as “C (volts)” \( \text{Data were plotted every 2 s from the recorder terminal averages, while the RS232 port printed out only once a minute.} \)

Analyzer C’s speed of response was excellent. While the test setup did not allow accurate measurements of analyzer-only response times, it did provide clear comparisons of relative response times among the three continuous, on-line TOC analyzers evaluated. Figure 9 represents the typical result. Analyzer C invariably gave the first indication of any change in the challenge concentration. Its response times \( (t_{r10}, t_{r90}, t_{f10} \text{ and } t_{f90}) \) varied somewhat with organic species and concentration, although transient responses and overshoots often complicated the determination of final steady state values. The procedure adapted was to determine a steady state value from a plot such as shown in Figure 9 by an eyeball best fit. This value then became the steady state value for determining the time to reach either the 10% or the 90% response levels. In many measurements of rise times, the initial TOC values were 1 – 2 ppb and for many fall times, the final TOC concentrations were also 1 – 2 ppb, representing the TOC concentration of the background UPW.

---

Figure 9. Representative Relative Response Times of the Test Analyzers
Analyzer C Response Times

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values deduced from the log (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t_{10} )</td>
<td>40 - 120</td>
</tr>
<tr>
<td>( t_{50} )</td>
<td>80 - 220</td>
</tr>
<tr>
<td>( t_{70} )</td>
<td>30 - 90</td>
</tr>
<tr>
<td>( t_{90} )</td>
<td>40 - 115</td>
</tr>
</tbody>
</table>

These measured response times are no doubt unique to the test setup used in this evaluation but probably represent the range of response times that would be encountered in an actual recycle system with mixed flows and feeds.

Analyzer C Percent Recovery

Analyzer C measures TOC “by converting organic carbon to organic acid” and relating the change in water conductivity brought about by the organic acids (delta conductivity) to the sample TOC. Analyzer C’s approach differs from that of other conductivity-based TOC analyzers in that it uses the properties of the initial and intermediate species formed during the reactions described in eq. (1) and does NOT wait until all these intermediates have been completely oxidized. Figure 1 shows that conductivity changes with time in the UV reactor, especially initially. Thus the tactic of measuring a delta conductivity after just a 15 s oxidation period, while allowing the rapid response observed, means that the relationship between delta conductivity and the sample TOC is species dependent. And, indeed, the manufacturer provides a number of different calibration curves from which one can select that curve which has been prepared for the specific organic compound in the water stream being sampled.

Unfortunately, in semiconductor water recycling, the compositions of the organic contaminants are usually unpredictable and unknown. Under these conditions, the selection of the right calibration curve or even an appropriate curve is guesswork. The strategy taken for this test series was to use the most sensitive calibration curve -- the curve that yields the highest value of TOC for a given value of delta conductivity. This strategy was assumed to mean that all errors in the measurement of TOC would be on the conservative, high side of the real TOC concentrations. Overestimating TOC and perhaps needlessly diverting recycle water was thought to be far more preferable than underestimating the real concentration and failing to divert water that should have been diverted. Less sensitive calibration curves were also used from time to time but offered no consistent advantage. The majority of the runs conducted during the evaluation were with the most sensitive calibration curve and only those are shown in this paper.

Unfortunately, the assumption that the most sensitive calibration would always overestimate the TOC proved not to hold for all the challenge analytes, introducing
significant uncertainty into the interpretation of TOC values measured when solutions are contaminated with unknown organic analytes.

Conductivity Effects and Limitations.

The TOC measurement of Analyzer C depends exclusively on the absolute value of delta conductivity -- the difference in conductivity between the conductivity sensor upstream (Sensor #1) of the UV reactor and the sensor downstream (Sensor #2) of the UV reactor. Interferences from changes in the concentration of conductive species besides those resulting from the oxidation of carbon will be reported as TOC if these conductivity contributions to each sensor are not perfectly synchronized in their arrival at the data processor. Analyzer C exhibited such interferences, primarily as spikes accompanying a change in the conductivity of the water sample. Figure 10 illustrates this effect. The challenge analyte for this run was 100 ppb sodium carbonate in water, a challenge analyte nominally containing zero oxidizable carbon but measurable concentrations of conductive species. Upon introduction of the sodium carbonate solution, one of the conductivity sensors detected the change in conductivity before the other. This timing means that a large conductivity difference signal, either positive (the signal reflecting the conductivity change reached the data processor from Sensor #2 before the signal from Sensor #1) or negative (opposite mismatch in timing) temporarily existed, producing the transient spike in the magnitude of the reported TOC. A believable, positive value of TOC was reported even though it bore no relationship to the concentration of TOC in the sample. Further evidence for this interference came from observing such spikes with the UV lamp turned OFF. UV irradiation is needed to oxidize the oxidizable carbon, so when it is not present these oxidizing reactions do not occur. Any TOC value reported in this operating mode is unrelated to the sample TOC. The data of Fig. 10 were, in fact, recorded with the UV lamp OFF.

When the injection of the challenge solution was stopped, a spike in TOC similar to that seen upon initiating the challenge reappeared in the data plot. Figure 11 is a blow up of this type of spike based on a test run similar to that depicted in Fig 10 but not the identical data. It shows that Analyzer C produced a TOC spike in excess of 100 ppb for nearly a minute while the other analyzers maintained the near zero values of TOC that are expected under this type of challenge. Figure 11 also clarifies the relationship between the two independent data records from Analyzer C. C(rs232) changes only every minute, repeating the same value when interrogated every 3-4 s during that minute. C(volts) is a plot of average TOC concentrations over 2 s intervals.
Figure 10. Start and Stop Spikes Induced by TOC-free Challenge Solution

Types of TOC Responses from Analyzer C

As noted earlier and as made clear by the manufacturer, the calibration of Analyzer C is species dependent. Accurate measurements of sample TOC can be expected only when the correct calibration curve for the specific organic contaminant in a water sample has been selected from among those available. Since this information is unlikely to be known with any certainty in recycle operations, the response of the analyzer to organics of concern was tested primarily using the most sensitive calibration curve. A number of response types have been identified after challenging the analyzer with the analytes listed in Table 1. The following paragraphs classify these response types.

Type 1: Conductivity spikes. This response is that just described in which conductivity changes independent of TOC generate transient spikes in reported TOC (Figs 10 and 11). The magnitude of the spike depends on the magnitude of the conductivity change. Challenge solutions of resistivity greater than about 10 MΩ-cm did not produce significant transient spikes. Below 1 MΩ-cm, the spikes could be large (> 100 ppb typically) and significant. Challenges with 100 – 400 ppb concentrations of Na₂CO₃, acetic acid and KHP produced such spikes. Adding 100 ppb of Na₂CO₃ to 100 ppb ethylene glycol introduced spikes into the response of this mixture, which, with just ethylene glycol alone, displayed the Type 2 characteristic illustrated in Figure 9 and more fully described next.
Spiking after turnoff of 100 ppb Na2C03 at 10:13:24

Type 2: Overestimation. This type of response (Figure 9) was the most common. The reported values of TOC were 1 – 4 times that of the other TOC analyzers, including the reference TOC analyzers. Operating with less sensitive calibrations generally, but not always, reduced the magnitude of the error. Among the analytes exhibiting Type 2 responses were methanol, IPA, MEK, acetone, ethylene glycol, F93 surfactant, OHS, sucrose, p-xylene, butyl acetate and amyl acetate. Most, but not all, high resistivity challenge solutions (resistivity > 15 MΩ-cm) gave this type of response.

Type 3a: Underestimation: negative delta conductivity. With some of the challenge analytes, even with the most sensitive calibration curve, Analyzer C underestimated the challenge TOC concentrations. Thus the magnitude of any TOC spike detected by Analyzer C can not always be assumed to be too high. Acetic acid is an organic to which the analyzer responded in this mode. Figure 12 shows that Analyzer C reported TOC values that were 60-70% of those reported by the other analyzers except during the period in which the startup, Type 1 conductivity spike dominated the reported TOC. For water of resistivity less than about 1 MΩ-cm, two distinct contributions determine delta conductivity: the Type 1 conductivity spike and the conductivity of the species created in the UV reactor. Acetic acid is an analyte which resulted in negative delta conductivities on passing through the UV reactor of Analyzer C. Negative delta conductivity means
that the water downstream of the UV reactor is less conductive than the water upstream of the reactor. This condition implies that conductive species in the upstream water have been reacted to form less conductive species that mask any oxidation of nonconductive, oxidizable carbon to CO₂. Organic acids typically exhibit this property.

The plot in Figure 12 makes the difference between the two sources of conductive contributions quite distinct. This clarity results from the fact that the two sources made contributions of differing sign and magnitude to delta conductivity. The TOC plotted rises rapidly initially, fall back to zero and eventually takes on an intermediate, stable value in which the Type 1 conductive contribution of non-TOC origin is the same to each sensor and delta conductivity reflects just the TOC contribution as designed. The sign of delta conductivity in the stable region was negative as previously noted. The sign of delta conductivity during the initial rise and fall was positive. The algebraic sum of the two contributions was initially positive but, as the Type 1 conductive contribution decreased, this sum decreased, passed through zero and took on the negative value characteristic of the stable challenge solution. Reported TOC, on the other hand, remained positive regardless of the sign of delta conductivity.

TMAH was another test analyte exhibiting similar behavior in that delta conductivity was negative. With this analyte, however, the less sensitive calibration curves yielded higher values of TOC than the most sensitive calibration curve. Differing times in the UV reactor explains this seemingly contradictory result. Flow rates with the low sensitivity calibrations are 20 mV/min rather than the 75 mV/min used with the most sensitive calibration. These slower flow rates imply longer times in the UV reactor. The longer time in the reactor for the lower sensitivity calibration produced higher absolute values of delta conductivity. Higher values of delta conductivity in turn corresponded to higher TOC values for this analyte even though the less sensitive calibration curve used converts any given value of delta conductivity into a lower TOC reading than the higher sensitivity calibration curve.

**Type 3b: Underestimation; positive delta conductivity.** Analyzer C also underestimated NMP concentrations but its response to NMP exhibited even more curious behavior. As shown in Fig. 13, the underestimation was pronounced at high concentrations (~900 ppb) but absent at lower concentrations (~90 ppb). Delta conductivity was larger at the low flows of the less sensitive calibration curves as was true in Type 3a behavior. However, the delta conductivity for an NMP challenge had a positive sign rather than a negative sign like the responses described as Type 3a.

Figure 13 shows that the TOC readings of Analyzer C are in good agreement with those of the other analyzers when the NMP concentration is ~90 ppb. At 900 ppb concentrations, however, Analyzer C underestimates the TOC concentration by a factor of 4-5 regardless of the calibration curve selected. This observation suggests that at the higher concentrations a smaller fraction of the oxidizable carbon has been reacted. NMP was the only example in this test series of a challenge analyte of high resistivity that did not exhibit Type 2 behavior.
Type 3c: Underestimation: concentration dependent sign of delta conductivity. Analyzer C also underestimated the TOC of KHP. Here again at the relatively low concentrations of ~100 ppb, Analyzer C agreed well with the other analyzers but significantly underestimated the TOC concentration when the challenge concentration was 400 ppb. The sign of delta conductivity was positive at the 75 ml/min flow rate but was negative at the 20 ml/min flow rate, suggesting that longer UV exposure allowed more of the conductive species in the upstream water to be converted into less conductive species (Figure 14).

Type 4: Gross Overestimation of TOC. Compounds that form conductive species under UV irradiation other than organic acids and CO₂ introduce changes in post irradiation conductivity that can be mistaken for oxidizable carbon. Chloroform is the primary example. A challenge solution of 100 ppb CHCl₃ was reported to have 4000 ppb TOC by Analyzer C. Chloroform, however, was the only analyte of those tested to show Type 4 behavior.
Figure 13. Degradation of Percent Recovery at Higher Concentrations of NMP (Analyzer C)

Summary, Analyzer C

One conclusion is that while Analyzer C is very fast in generating a TOC reading, the interpretation of that reading remains species dependent. In the absence of species information, however, an observer does not know whether a reading is too high, too low or even related to TOC concentration. What corrective action to take other than to further investigate the cause of an abnormal reading or an excursion remains unclear. In some operations a rapid response alone may be very valuable. In others, such as water recycling systems with constantly varying water resistivity, the large resistivity-dependent signals may obscure or totally mask the TOC concentrations of interest. This high sensitivity to changes in resistivity could make Analyzer C attractive as a final check of recycled water quality on the assumption that if the water is stable enough to not generate TOC spikes, it’s probably free not only of TOC but other objectionable species as well. Still, the fact that the TOC of water containing certain analytes of concern, such
as NMP, can be significantly underestimated implies some finite risk to using Analyzer C as a stand alone TOC analyzer for judging the quality of recycled water.

![Oxidation Characteristics](image)

**Figure 14. Dependence of Delta Conductivity on Concentration and Time of Oxidation**

**Conclusions**

One of the primary purposes of this evaluation was to measure performance parameters of Analyzer C, a newly introduced product, and to assess its role in the recycling of spent rinse waters in semiconductor manufacturing facilities. Comparisons with the latest versions of competing commercially available TOC analyzers were also part of the evaluation. Analyzer B, the analyzer recommended for the recycle role in the 1996 evaluation, was part of this new evaluation as was Analyzer A which also participated in
the 1996 evaluation. All 3 of these analyzers are on-line analyzers with sub 5 minute response times and can measure the TOC concentration in a water stream continuously with no off-line interruptions.

Response Time

Of the three continuous, on-line analyzers, Analyzer C had the fastest response times by far. Water flow rate to this analyzer was somewhat faster than to the other two and water flow rate through the analyzing section was an order of magnitude higher. These high flow rates produced rapid detection of changes in differences between the conductivity of the incoming water and the water exiting the UV reactor. All such changes in conductivity were attributed to the formation of conductive species from oxidizable carbon in the water sample and were converted to concentrations of TOC by selecting that calibration curve developed for the specific oxidizable carbon compound of the water sample. The fact that one is unlikely to know the composition of the oxidizable carbon in his recycle water and hence be unable to pick the “right” calibration curve was addressed in this evaluation by selecting the most sensitive calibration curve for most of the data collection.

The response times of Analyzer B probably reflected performance similar to that measured in the 1996 evaluation, although the values reported here are slightly longer. In 1996, a grab sample technique was used in which a short feed line connected to the grab sample inlet port was switched from one flask to another to simulate a step change in TOC concentration. The test configuration used in this evaluation series used longer feed lines and mixers with additional instrumentation between the analyte injection port and the analyzer inlet. In addition to longer transit times between injection and analyzer inlet, the mixing smeared the shape of the step in concentration and made it more diffuse. However, the present configuration allowed more realistic and accurate comparisons of the response times of the three analyzers, since all were supplied from a common feed source of water.

Analyzer A responded slightly faster this time than Analyzer B. This conclusion held even when both analyzers operated without their TIC removal stages in-line. But again both Analyzers A and B had response times that were 4 - 6 times slower than Analyzer C.

Percent Recovery

Percent recovery describes how accurately the TOC analyzer represents the actual concentration of the challenge analyte. With the exception of the volatile organic challenges, both Analyzers A and B had recovery efficiencies of 100% +/- 30%. This result closely matches that reported in the 1996 evaluation. On the other hand, it was the exception rather than the rule when Analyzer C, as operated in this study, exhibited recovery efficiency in this range. What was worse was that the recovery efficiency could be either too high or too low and that significant transient responses were generated by mildly conductive water samples. Analyzer C's very impressive response times were counterbalanced by very unimpressive percent recoveries – so much so that the term
percent recovery is hardly useful in categorizing its output signals. The hope that the user could select the most sensitive calibration curve and rest assured that the reported TOC concentration represented the maximum value of the actual TOC concentration was dashed early in the evaluation. While many of the challenge analytes did, in fact, react in accordance with this hoped for behavior, many others did not. The concentration of these other organic analytes could be grossly underestimated even when the analyzer was set up with its most sensitive calibration curve.

Analyzer C generates an output signal based on the absolute value of differences in the water conductivity measured by the cells upstream and downstream of the UV reactor. The sign of the conductivity difference does not affect the calibration; no trend information is utilized. The absolute value of conductivity difference measured over a fixed time displacement is the sole data used to calculate TOC from the calibration curves at one of two preselected sample flow rates. This simple approach yields very fast responses, clearly the direction sought by water recyclers. However, Analyzer C has probably pushed too far in that direction; a better tradeoff would be one that uses additional input data and analyses to make the analyzer response more discriminating and useful, even at the cost of some added response time.

The more practical course of action for most recyclers is to choose one of the other two TOC analyzers evaluated (Table 2). Analyzer B should be operated with an upstream ICR and the Analyzer A should be run in its TOC mode. Volatile organics will thus be underestimated by each of these TOC analyzers but because of the very property that makes these organic difficult to retain in a TIC removal module, they should be easily removable by conventional water treatment technology.

Reference


Acknowledgements

Vendor support of this evaluation was outstanding. Each provided a test analyzer and guidance for the test series. They not only made the evaluation possible but also much easier than it might otherwise have been.

The evaluation was sponsored jointly by EPA, SEMATECH and DOE and conducted at Sandia National Laboratories, Albuquerque, NM. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the DOE under Contract DE-AC04-94AL85000
<table>
<thead>
<tr>
<th>Spikes</th>
<th>Overestimate</th>
<th>Underestimate</th>
<th>Gross Overestimate</th>
<th>Recycle Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl</td>
<td>Acetone</td>
<td>Eth Gly</td>
<td>Acetic Acid</td>
<td>Chloroform</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>IPA</td>
<td>FC93</td>
<td>KHP</td>
<td>Limited</td>
</tr>
<tr>
<td>ρ &lt; 1 MΩ·cm</td>
<td>OHS</td>
<td>MEK</td>
<td>NMP</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Amyl Acetate</td>
<td>Sucrose</td>
<td>TMAH</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Butyl Acetate</td>
<td>Phenol</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Analyzer A**  
( TOC MODE )

**Analyzer B**  
( ICR in-line )

100% +/- 30%  
Underestimate  
Recycle Use

All except the volatiles  
(see next column)  
Amyl Ace CHCl₃  
p-xylene C₆H₁₂  
Butyl Ace* MEK*  

*Analyzer B

Yes