

The Performance Comparison of Ultrapure Water TOC Analyzers using an Automated Standard Addition Apparatus

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Abstract

Improvements in ultrapure water technology have driven the typical level of TOC in semiconductor process water to less than 5 ppb. The performance of commercially available TOC analyzers at these low levels of TOC has never been characterized. It is not known how well low level on-line TOC analyzers can measure the likely organic compounds that may be found in UPW.

We have applied an on-line standard addition apparatus in a field study of UPW systems to answer these questions. The details of this apparatus were discussed in the 1999 SPWCC. Four different ultrapure water TOC analyzers, Anatel A1000, Anatel A1000XP, Sievers Model PPT, and the Thornton 502P were studied. When very low levels of dissolved oxygen or high levels of dissolved hydrogen were present in the tested UPW, a Sievers 800, with internal oxidizer addition, was used to assure the accuracy of the standard additions.

Nine organic compounds were selected based on the likelihood of their presence in UPW or their chemical similarities to compounds that are likely to be present in UPW. The compounds studied included trimethylamine (anion resin), benzenesulfonic acid (cation resin), IPA (source water and bacterial metabolic waste), urea (source water), sucrose (small easy to oxidize organic), glycidol (reclaim water), TMAH (reclaim water), 1,3-

dichloro 2-propanol (analog for chloroform), chloroform, and mixtures of these organic compounds.

The study was conducted at five different semiconductor sites. The UPW sources at these sites varied in dissolved oxygen levels from 25 ppb to zero ppb. One site had high levels of residual H₂ in solution. The water and ambient temperatures at most sites was about 25 degrees °C, one site temperature water and ambient temperature was 32 °C.

The data from these tests are examined and compared. The surprising results of the study are discussed and analyzed.

Introduction

It is not unusual to find unexpected analytical performance characteristics when operating an analyzer at or near the limits of it's detection. Factors such as environment temperature, sample contamination, calibration stability, electronic noise, software algorithms, can all contribute to analytical instrument problems in its most sensitive applications.

Ultimately, it is up to the user of the equipment to validate its operation in the actual operational environment, but these efforts are frequently limited by equipment, fiscal or time constraints.

It was the objective of this scientific study to provide unbiased and useful information about the operational characteristics of ultrapure water TOC analyzers in these real environments. We developed an automated device that accurately and precisely introduces ppb and sub-ppb chemical standards to an ultrapure water stream for analysis by different TOC analyzers. This automated standard addition apparatus was described in a 1999 SPWCC paper by Godec et al. (1). We invited semiconductor manufacturing companies to participate in an open testing program to measure the operational characteristics of commercially available online ultrapure water TOC analyzers. The testing reported in this paper was performed in 1999.

The study was conducted at five different semiconductor manufacturing plants, three of the manufacturing factories were in the United States, one was in Korea, and the last one was in Japan. Five types of TOC analyzers were tested, four of which were reagentless (A-1000, A-1000XP, 502P, and PPT) and one that uses reagents (Sievers 800). Two

different standard addition devices produced standard additions of nine different pure organic compounds at from 1 to 5 different concentration levels and three mixtures of organic compounds at from 1 to 3 different concentration levels. The total number of experiments conducted was 297.

Operator Bias Controls

All selected companies agreed in advance to provide a technical observer to review the testing protocol, testing procedures, data, and data analysis for correctness and validity. Ionics Sievers provided a chemical engineer or chemist, concentrated standards, and a standard dilution device. The testing required from one to two weeks at each site. Each volunteering company received the raw data, data calculation spread sheets, and a final report for their own internal use. Selection of test compounds and TOC analyzers was decided by the semiconductor companies with input from Ionics Sievers.

TOC Analyzers Tested

The analyzers tested in this project include four different reagentless ultrapure water TOC's and a reagent based TOC analyzer. Almost all the TOC analyzers tested were supplied by the testing site facility. A total of 17 different TOC analyzers were used. One of the Thornton 502P's was tested at two different test sites.

Testing the Accuracy of TOC Measurements

Absolute TOC accuracy is determined by two major factors, the complete recovery (100% response factor) of all organics in the water sample and any TOC contributed by the TOC analyzer (TOC offset correction).

A TOC instrument response factor of 100% for any organic compound is an important requirement for verifying the correct measurement of TOC in UPW. To develop a test for the proper operation of a TOC analyzer, a method to determine organic recovery is required. Because it is not known if the TOC analyzers to be tested measure all organics equally well, a knowledge of the organic composition of a water sample is required to provide a good test for correct TOC response for that sample. It is very difficult to qualify and quantify sub-ppb levels of organics in UPW and this information is generally not known for a given sample. If we selected the chemicals that are likely to be present in an ultra pure water sample, then we can challenge the TOC analyzers with additions of these compounds and check the analyzer recovery for each. If the recovery is acceptable

for each of the compounds in the customers UPW then it can be assumed that the TOC analyzer is responding correctly to any changes in TOC in the ultra pure water.

With a TOC offset correctly set and when the ultrapure water has zero organics in it the analyzer should read a TOC of zero. We have produced TOC water with an estimated concentration of 0.08 ppb TOC at Sievers (3). Unfortunately, it is very difficult to make absolute zero TOC water and this was not attempted for this project. The reagentless Ionics Sievers PPT analyzer TOC offset is determined by turning off the UV oxidation light and adjusting the reading to zero. The Ionics Sievers model 800 TOC analyzer adds two reagents, so the TOC is measured in each reagent, the UV oxidation light is turned off and the blank is measured, and the three measurements are used to find the correct TOC offset. It is not known how the factory TOC offset was determined with the other TOC analyzers. Therefore, the zero offset was assumed to have been determined and calibrated at the manufacturer's factory.

Criteria for UPW Organic Compound Selection

To make the selection of organic compounds as realistic as possible, a list of requirements was developed.

- 1) Any compound added to the UPW must not lower the resistivity by more than 0.25 Mohm-cm. Assuming an initial water resistivity of 18.24 Mohm-cm, the resistivity should stay between 18.3 and 18.0 Mohm-cm during the addition of any compound.
 - a) In 1991 Kevin Pate showed that low concentrations of basic compounds can be added without changing the conductivity (4).
 - b) Reagentless TOC analyzers require deionized water or deionized water with a single known ionic contaminant, such as CO_2 or NaHCO_3 , to operate properly.
- 2) There should be a high probability that the selected compound actually exists in ultrapure water. Such compounds may come from water purification system components, feed waters, biological surface growth metabolic waste products, organics from purge or blanket gases, and rinse water reclaim sources.

Organic Test Compounds

Ion exchange resins are clearly a source of low level TOC(2). We have demonstrated this at our laboratory in Boulder when creating ultra low TOC water (3). Other groups have detailed the compounds that may be extracted in ultra low levels. Frances Cutler with

Southern California Edison examined cation resin extractables (5). Anion exchange resins are known to release some of the basic amine functional group into UPW at very low concentrations (6). Urea is another candidate organic likely to be present in ultrapure water (7). Urea is often found in UPW plants using surface waters down stream of municipalities as feed water. Urea is non-ionic, difficult to oxidize, very polar and has a low molecular weight. All of these properties allow at least some of it to pass through a water purification system. There is strong evidence that organic nitrogen compounds such as urea or amines are present in UPW systems. In a paper presented at the 1999 Semiconductor Pure Water and Chemicals Conference, Tetsuo Mizuniwa et al. show that organic nitrogen is found in part per billion concentrations in the selected ultrapure water systems (8). The data in their paper (Table 4 found in ref.8) in combination with the reasonable assumption that each organic nitrogen has at on average at least two carbon atoms associated with it, suggests that one should expect to find 0.13 ppb to 1.66 ppb of TOC contributed only from the organic nitrogen compounds (Table 1).

Table 1: Expected TOC from Measured Organic Nitrogen in UPW Systems

	Organic sourced NO ₃ ⁻ (ng/L concentration units)	Expected TOC assuming two Carbon atoms per each organic Nitrogen atom (ppb as C)
System A	1,900	0.73
System B	910	0.35
System C	3,300	1.28
System D	1,600	0.62
System E	340	0.13
System F	4,300	1.66

Table created from data shown in table 4 of reference (8).

Low molecular weight alcohols are also likely to be found in UPW. Other authors (9) suggest biofilms may contribute organics both as a metabolic waste (alcohols such as ethanol) and amino acids (methionine and glycine) produced from cell breakage (lysis). There is clear evidence that chlorinated and brominated hydrocarbons are often present in final polished UPW (10).

Another source of organics is created when UPW recycle systems are introduced. These compounds are easy to identify, as they are the organic compounds used in the semiconductor manufacturing process (11). Of these reclaim organic compounds IPA and acetone (alcohols and ketones) are the most common. Organic surfactants may have lower removal efficiency in the recycle water treatment process than other reclaim organics. Suitable surfactants to study are Triton X-100, Wako NCW-601, FC-93 (surfactant), and glycidol (Olin Hunt surfactant). Other reclaim organic compounds that would be useful to test include ethylene glycol, cyclohexanone, and TMAH (11). The compounds selected and the selection criteria for each are listed in Table 2, below.

Table 2: Proposed Organic Compounds for Injection into UPW Systems

Compound	Selection Criteria	Suggested Test TOC Concentration (ppb as C)
IPA (Isopropanol) $\text{CH}_3\text{CHOHCH}_3$	Reclaim (10), Bacterial Metabolic Waste (9)	0.156, 0.312, 0.625, 1.25, 2.5, 5.0
Sodium Benzenesulfonate $\text{C}_6\text{H}_5\text{NaO}_3\text{S}$	Cation resin extractable organic (4)	1.25
Trimethylamine (TMA) $(\text{CH}_3)_3\text{N}$	Anion resin extractable organic (5)	0.25, 1.25
Urea H_2NCONH_2	Surface feedwaters (6)	0.156, 0.312, 0.625, 1.25
Glycidol $\text{H}_2\text{COCHCH}_2\text{OH}$	Reclaim surfactant	1.25
Tetramethylammonium Hydroxide (TMAH) $(\text{CH}_3)_4\text{NOH}$	Reclaim Organic (11)	1.25, 2.5
1,3-Dichloro 2-propanol (DCP) $\text{CH}_2\text{ClCHOHCH}_2\text{Cl}$	Chlorinated Organic (10)	1.25, 2.5, 5
Chloroform CHCl_3	Chlorinated Organic (10)	0.25, 0.5, 1.0, 2.0
Sucrose $\text{C}_{12}\text{H}_{22}\text{O}_{11}$	Easy to oxidize organic for low level linearity testing	0.156, 0.312, 0.625, 1.25
Urea/TMA/ Sodium Benzenesulfonate	Resin organics and urea mixture.	1.5
IPA/Glycidol/TMAH	Reclaim mixture	1.5
TMA/IPA/DCP	Random Mixture	0.25, 0.625, 1.25

Statistical Sampling Parameters on TOC Additions

The TOC background of the UPW to be tested is measured first. Then the standard addition device is activated and a step change is produced in the background TOC level. This delta TOC change from the baseline TOC level reflects the TOC analyzers response to a known concentration of an organic standard. The stability of this baseline is important to achieve good low level TOC additions. Some of these experiments used a reference TOC analyzer to monitor the stability of the baseline TOC.

All measurements of TOC step changes have a sample population of at least 5 data points after stabilization is reached. All baseline measurements have sample populations of at least 5 TOC measurements.

Percent Recovery Calculation

The percent recovery (%R) calculation is made by recording the average stabilized TOC response (R) subtracting the average baseline TOC response (B) and dividing this by the expected TOC change (E) (as determined by the dilution device) and finally multiplying this result by 100. The equation is $\%R = ((R-B) / E) * 100$.

Estimated Error in the Addition Standards

The flow meter in the dilution devices measures the dilution water flow rate (F) to an accuracy of $\pm 1\%$. The syringe flow rate (S) is accurate to $\pm 1\%$. The concentrated standards (C) were mixed up to an accuracy of $\pm 1\%$. The dilution concentration is equal to $C * S / F$. The final diluted chemical concentration is estimated to be accurate to $\pm 1.7\%$, based on standard propagation-of-error analysis (12). An additional error of $\pm 2.5\%$ is assigned to the measurement of the water baseline TOC reading before and after the change in TOC from the injection. Therefore, the total error in the diluted standard that flowed into the test TOC's was estimated to be about $\pm 3\%$.

Experimental Results

The data and results from five testing sites will be discussed.

Test Site: Colorado, USA

At this location four organic compounds were used to challenge four different TOC analyzers. The analyzers studied included Anatel's A1000, Thornton's 502 P, the Sievers PPT, and a Sievers 800.

Compounds tested and their test concentration are shown in Table 3.

Table 3: Compounds Tested at the Colorado, USA Study Site.

Compounds Tested	Test Concentrations (ppb as Carbon)
IPA	0.312, 0.625, 1.25, 2.5, 5.0
Sucrose	0.156, 0.312, 0.625, 1.25
Urea	0.312, 0.625, 1.25, 2.5, 5.0
Chloroform	0.25, 0.5, 1.0, 2.0

The ultrapure water at this site had a D.O. concentration of 5 ppb. The testing setup is shown in Figure 1.

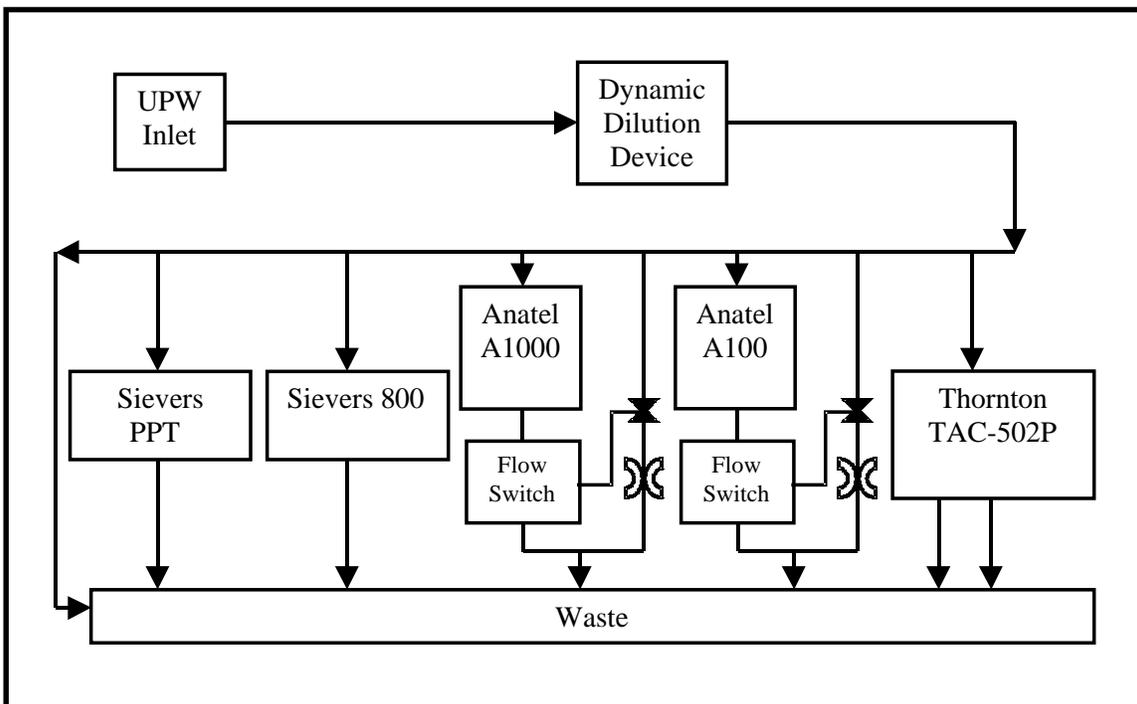


Figure 1: The Apparatus Setup at the Colorado Study Site.

The flow rates through the analyzers were set to 125 ml/min, except the flow through the Thornton 502P which was set to 230 ml/minute. The Thornton was a new instrument just

out of the box. It was calibrated with the factory recommended calibration curve for ultrapure water (curve # 1 and 75 ml/min.). The 502P UV lamp was 175 hours old.

The A1000 showed no errors during testing, but it was not known how many operating hours were on the UV lamp. The Model 800 was prepared for low level operation. We will not discuss the A100, as this product is no longer supported by Anatel. Both Anatels, A1000 and the A100 were operated with flow bypass devices to keep the total flow rate through the dilution device constant.

The results of the additions are displayed in the following charts 1-6. Charts 1 and 2 show the response from two easy to oxidize compounds. The most interesting charts are charts 3 and 4. They show that the Thornton and the A1000 are not responding to urea (chart 3) and showing very high responses to chloroform (Chart 4). In Chart 5 a statistical estimation of the precision is shown in a standard addition graph of the instrument responses to sucrose (13-17). The precision of the PPT, Sievers 800, and 502P are very good, especially considering the very small amounts of sucrose that was added. The Thornton appears to be recovering only about 42% and the A1000 is recovering around 88% of the expected sucrose TOC change.

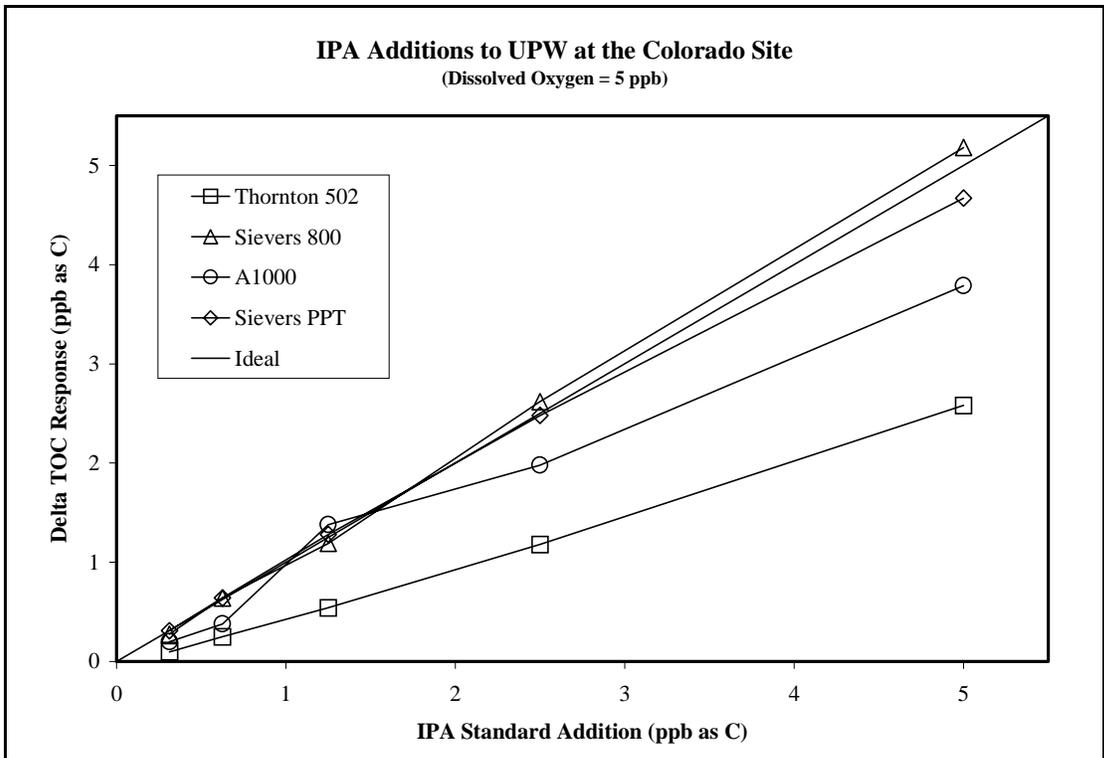


Chart 1: IPA Additions and TOC Responses at the Colorado Site.

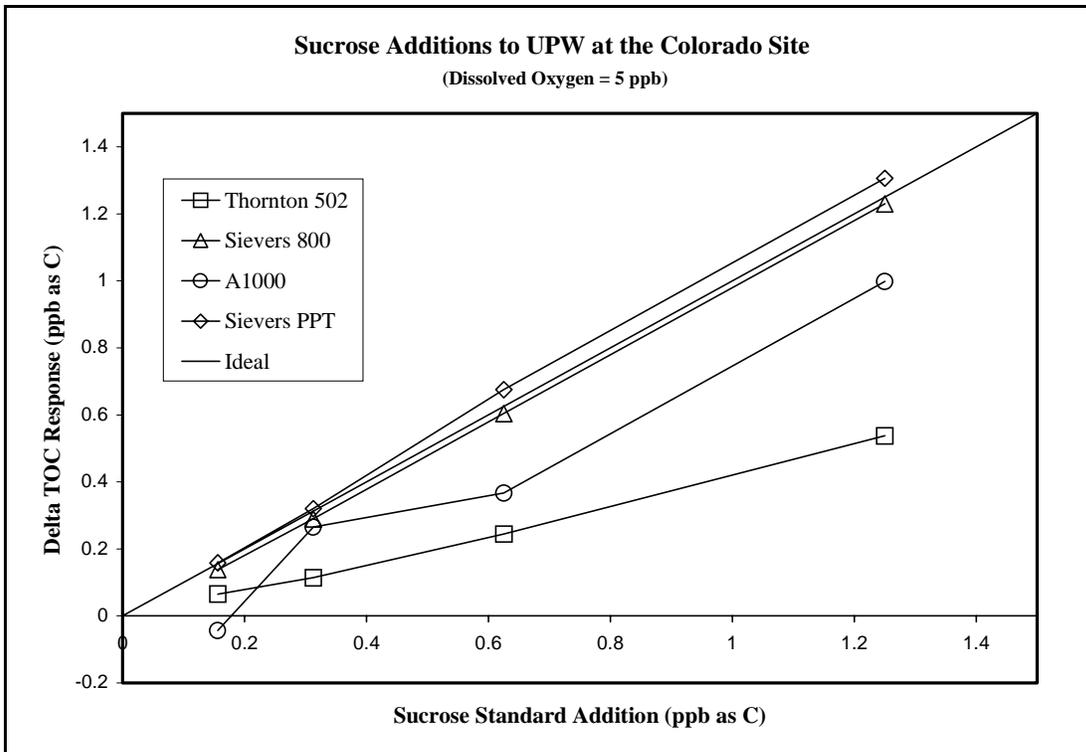


Chart 2: Sucrose Standards Additions and TOC Response at the Colorado Site.

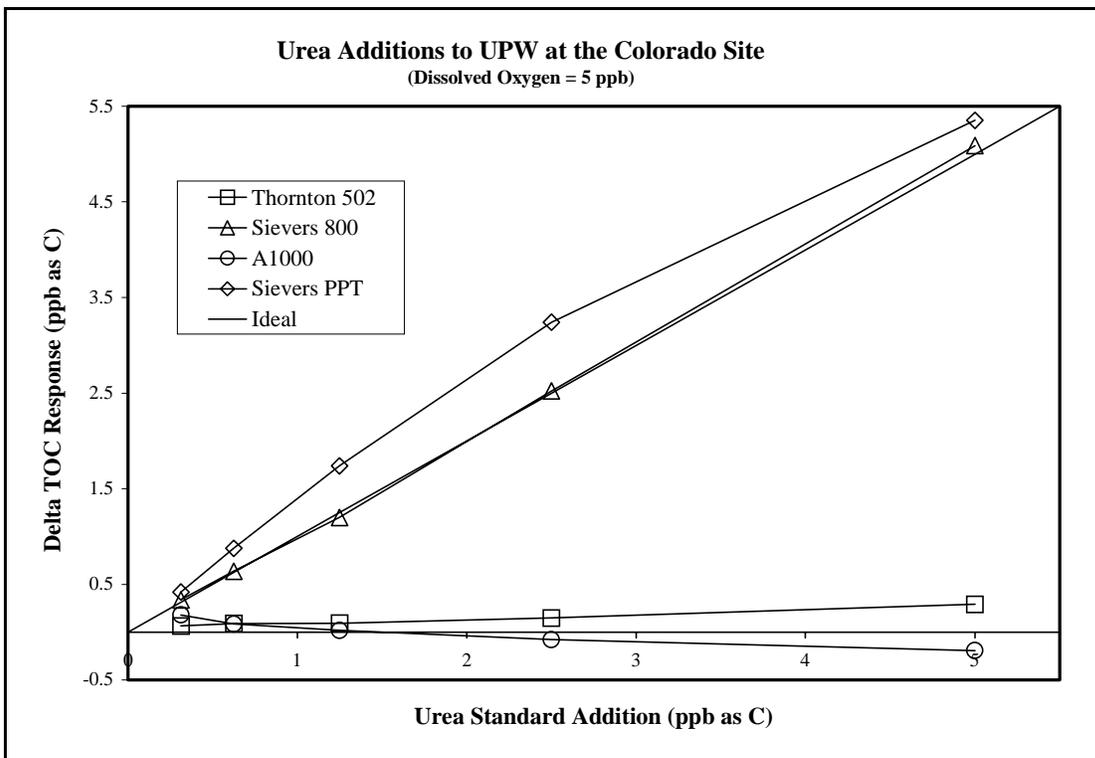


Chart 3: Urea Addition and TOC Responses at the Colorado Test Site.

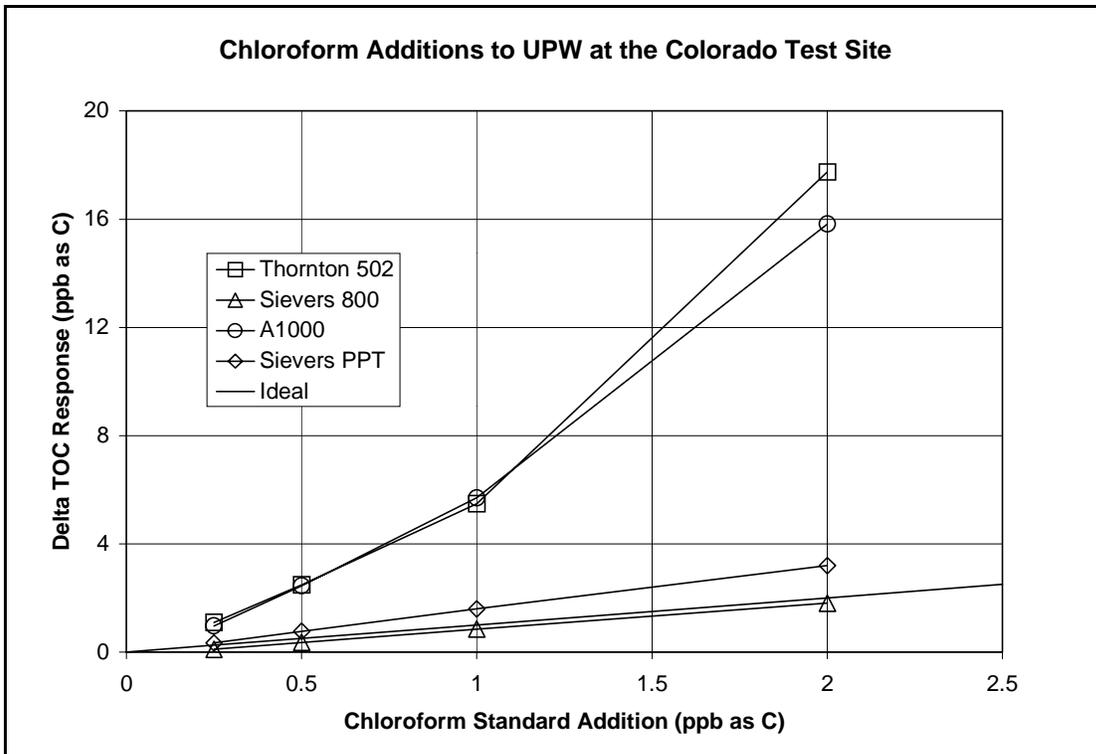


Chart 4: Additions of Chloroform and TOC response at the Colorado Site.

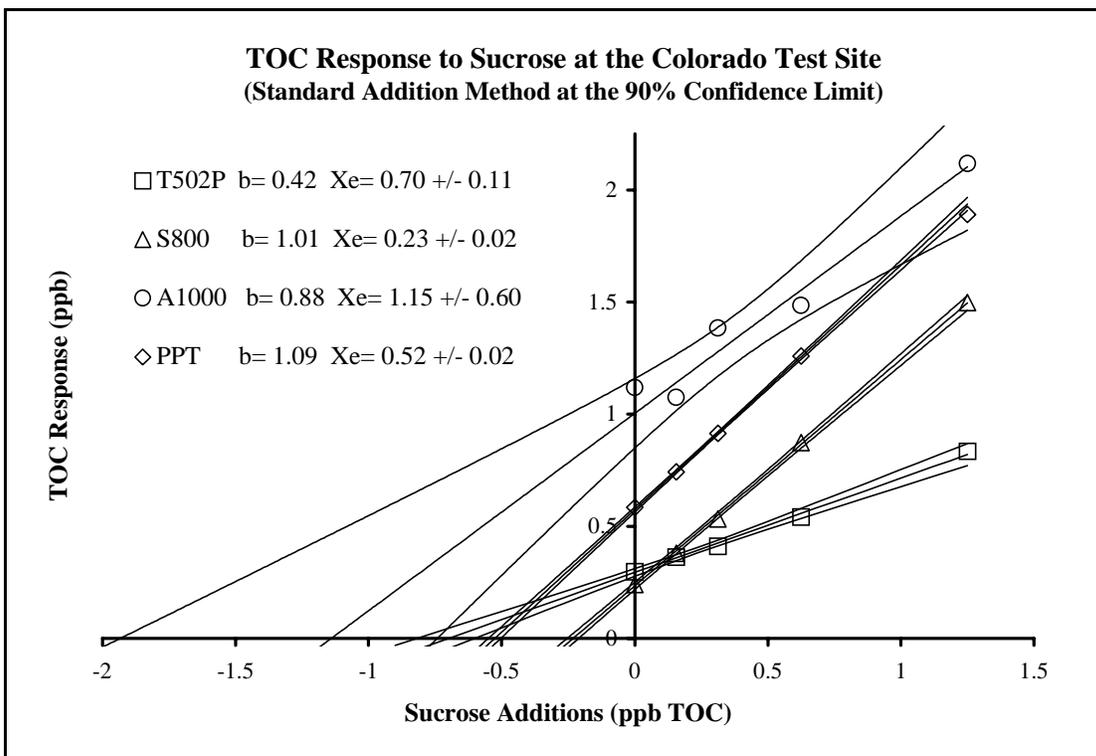


Chart 5: Standard Addition Method on Sucrose at the Colorado Test Site.

A summary bar chart (Chart 6) shows the overall average response of each organic compound as a function of the different TOC analyzers.

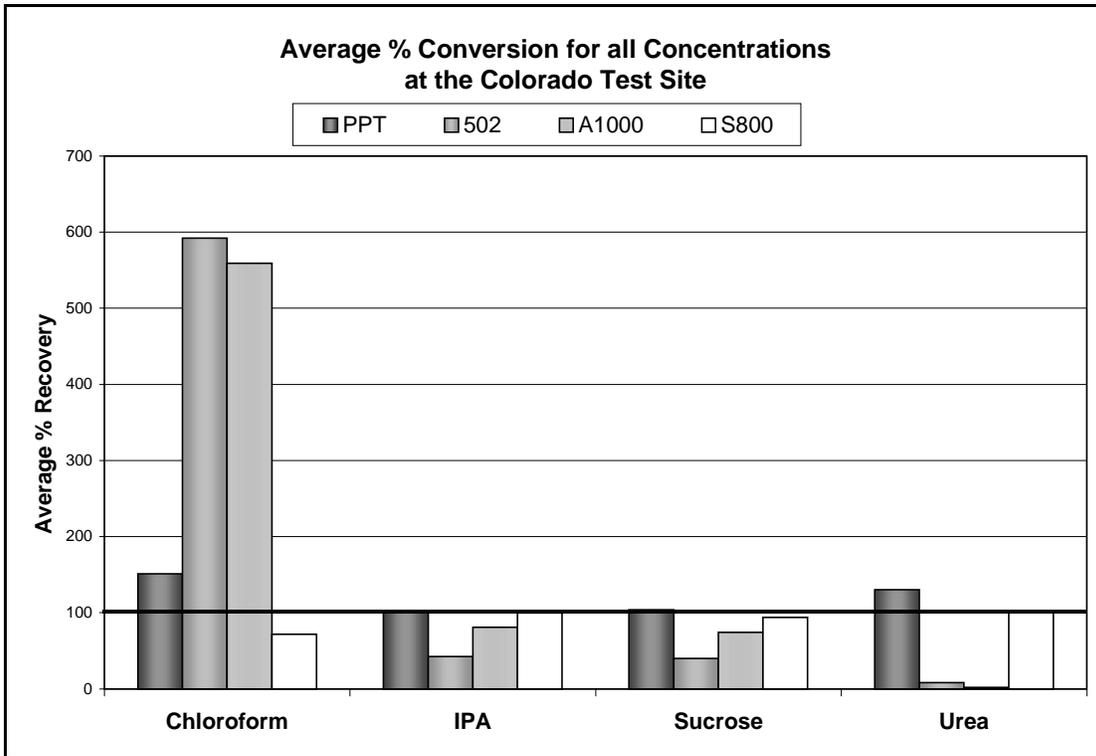


Chart 6: Average Conversion of all Concentrations at the Colorado Test Site.

The Sievers model 800 and Sievers “PPT” show results closest to 100% for all of the compounds tested. The chloroform caused high readings in the Thornton 502P and the Anatel A1000. This is explained by the formation of chloride ions that are measured as HCO_3^- ions (10). The very low urea recovery for the Thornton 502P and the Anatel A1000 is not understood. The 502P was set up per the manual for operation on ultrapure water. Under these conditions the 502P is operated at a UV reactor residence time of 15 seconds (at 75 ml/min.) and recovers 5.8% of the urea TOC. When the flow rate is decreased to 25 ml/min. and the UV reactor residence time increased to 45 seconds the percent recovery increases to 33%. This strongly suggest that the Thornton 502P when operated at the recommended UPW setup conditions (75 ml/min. reactor flow rate) does not have enough UV light exposure to completely oxidize the urea to CO_2 . The A1000 recovery on urea is even lower, suggesting that it also does not achieve complete oxidation under normal operational conditions.

Test Site: Oregon, USA

At this semiconductor manufacturing site we tested seven organic compounds and five different TOC analyzers. The analyzers studied include four reagentless TOC's the Anatel A-1000, Anatel A-1000XP, Thornton 502P, and the Sievers PPT. The fifth analyzer is a reagent based Sievers model 800, setup for low TOC operation. The model 800 data are not reported here. The compounds tested and the concentrations are shown in Table 4.

Table 4: Compounds Tested at the Oregon Study Site.

Compound	Concentration (ppb C)
Urea	0.15625, 0.3125, 0.625, 1.25
Trimethylamine	0.25, 1.25
Benzenesulfonic Acid	1.25
Isopropyl Alcohol (IPA)	0.15625, 0.3125, 0.625, 1.25, 2.5
Glycidol	1.25
Tetramethylammonium Hydroxide (TMAH)	1.25, 2.5, 5.0
1,3-Dichloro 2-propanol	1.25, 2.5
Urea/Trimethylamine/ Benzenesulfonic acid	1.5
IPA/Glycidol/TMAH	1.5

The water properties at this site are shown in table 5. It includes the average level for each parameter measured during the standard addition testing.

Table 5: Average Water Quality Parameters at the Oregon Study Site.

UPW Parameter	Average Levels Measured
Resistivity (M Ω -cm)	18.3
PPT TOC (ppb)	0.75
Reactive Silica (ppb)	0.68
Dissolved O ₂ (ppb)	25
Temperature (°C)	24.5

The arrangement of the test equipment is shown in figure 2.

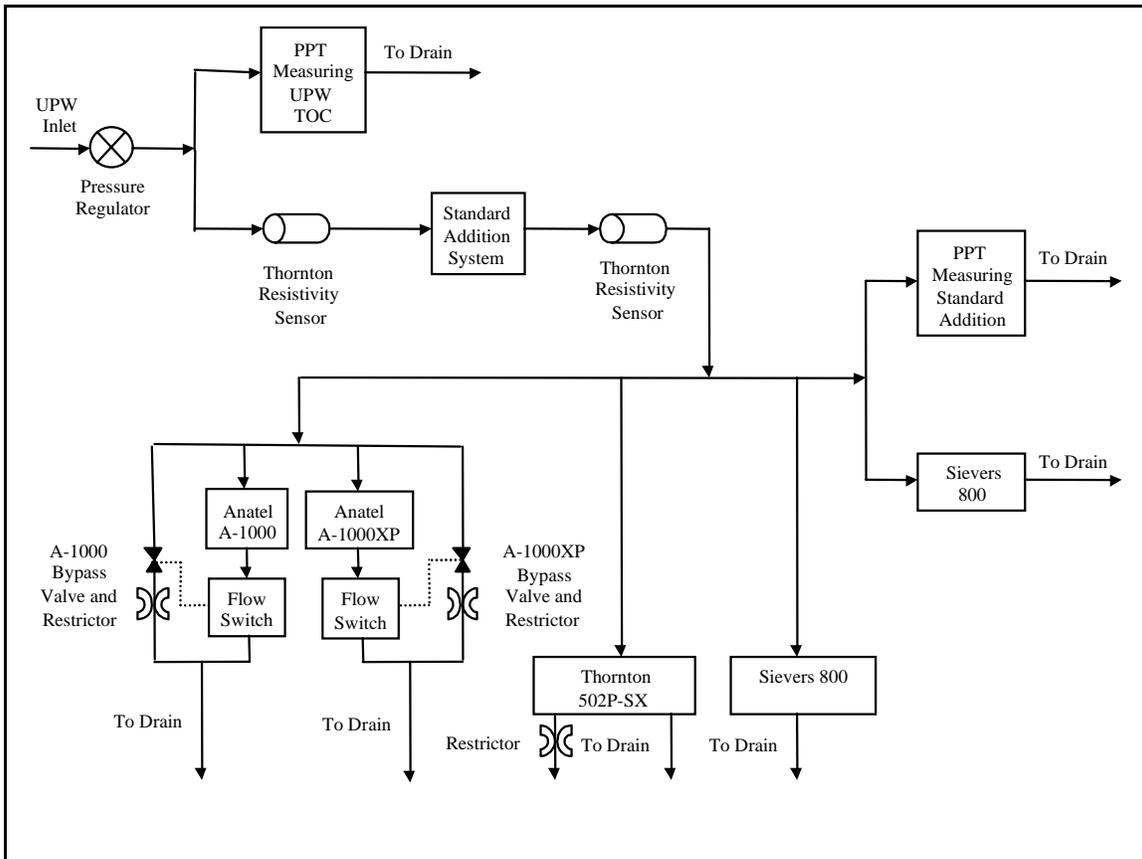


Figure 2 : Apparatus Setup at the Oregon Test Site

An additional PPT was used to track the TOC level of the UPW to correct the TOC response of each analyzer in the event the UPW TOC changed during the standard addition testing. The pressure regulator was used to regulate the inlet pressure to 20 psig. The Thornton sensors were used to measure the resistivity change associated with each standard addition.

The PPT's were supplied by the Test Site and had UV lamps that were nine months old out of a one year operating lifetime. They were setup to run in *Analysis* mode. The flow rate measured from the output of the PPT's was approximately 110 mL/min for each.

The A-1000 was supplied by the Test Site and its UV lamp was 5 months old. It was setup to run *Auto TOC* mode. A bypass loop was installed on the A-1000 to limit the change in sample flow when the A-1000's internal valve opened and closed. The bypass was controlled by a flow switch that sensed the stoppage of flow in the A-1000 and opened the bypass valve. The bypass restrictor was set to match the pressure drop of the

A-1000. By limiting the change in sample flow, the interference to other analyzers and to the standard addition system was also limited. The flow rate measured from the outlet of the A-1000 was approximately 350 mL/min.

The A-1000XP was a demo unit on loan to the Test Site. The age of its UV lamp was unknown. Following the instructions in the manual for optimal operation, the A-1000XP's sample time was set to three minutes and its *Valve@Idle* setting was set to "Open" to permit continuous flow through the instrument. A bypass loop was installed on the A-1000XP, but since the A-1000XP was operating with continuous flow, it was not required. The A-1000XP was setup to run in *Auto TOC* mode. The flow rate measured from the outlet of the A-1000XP was approximately 350 mL/min.

The 502P-SX was also a demo unit on loan to the Test Site and the age of its UV lamp is unknown. This 502P had the same serial number as the 502P used at the Arizona test site. The unit was setup the same as in the 502P used at the Colorado test site. Following the instructions in the manual for optimal operation, the algorithm curve used for TOC measurement was set to "1" which is the curve corresponding to ultrapure water. This curve requires the sample flow rate to be set at 75 mL/min. Consequently, the sample flow rate was adjusted to 75 mL/min by means of the flow adjustment screw. There are two outlets from Thornton 502P-SX, the oxidized sample outlet and the sample bypass outlet. A restrictor was placed on the sample bypass outlet to help achieve specified operating flow rates of other analyzers. This restrictor did not affect the sample flow rate through the 502P-SX, which remained at 75 mL/min. This was confirmed by measurement of the oxidized sample flow rate. The sample bypass flow rate was measured at approximately 75 mL/min. The 502P-SX was put into *Measure* mode.

The experimental procedure used at this site and the following sites is described as follows. The compounds requiring multiple concentration measurements were run using a stair step approach as shown in figure 3. The highest concentration was run first, the next highest level run second, etc. This approach is efficient and was made possible by the use of the PPT measuring the TOC of the incoming UPW. Without it, the UPW TOC would have to be measured by each analyzer before each standard addition which would greatly increase the amount of time required to complete all of the testing.

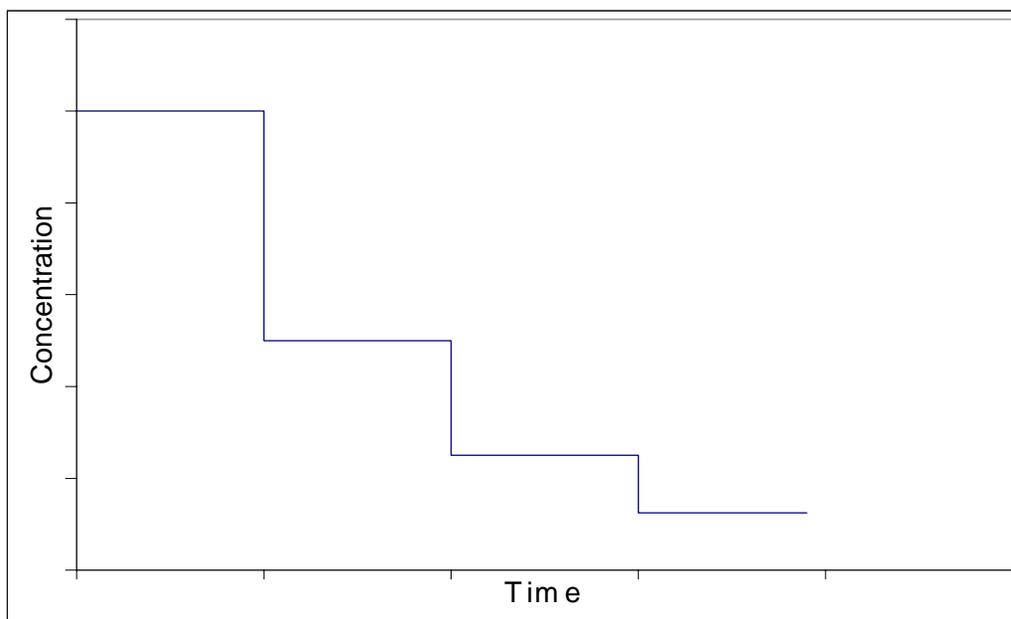


Figure 3: Stair Step Approach to the Standard Addition of a Compound at Multiple Concentrations.

The analyzers were run overnight to allow them to completely rinse down before any standard addition testing was performed. This was repeated each night to allow the analyzers to rinse down before testing started the next day. During the testing, data was taken every eight minutes which coincided with the analysis time for the PPT. The data recorded consisted of the resistivity measured by the two Thornton sensors, the TOC and resistivity measured by the A-1000, A-1000XP, and the 502P-SX, the TOC, TOX, and resistivity measured by both PPT's, and the TOC, TC, and IC measured by the 800's.

Each morning at least one hour of data was taken before the standard addition testing began to get UPW TOC data from each analyzer. Before testing began, the standard addition system syringe and injection lines were flushed with standard three times to ensure that the syringe and injection lines only contained standard. After the injection had started, the TOC measurements of each analyzer were allowed to stabilize. The testing for a particular TOC step change concluded when at least five data points were stable for each analyzer. After the testing of a compound had been completed, the standard addition system syringe was flushed three times with UPW to ensure that the syringe and

injection lines were clean. The standard addition system syringe and injection lines were flushed with the new standard as described above before the next test began.

Isopropanol (IPA)

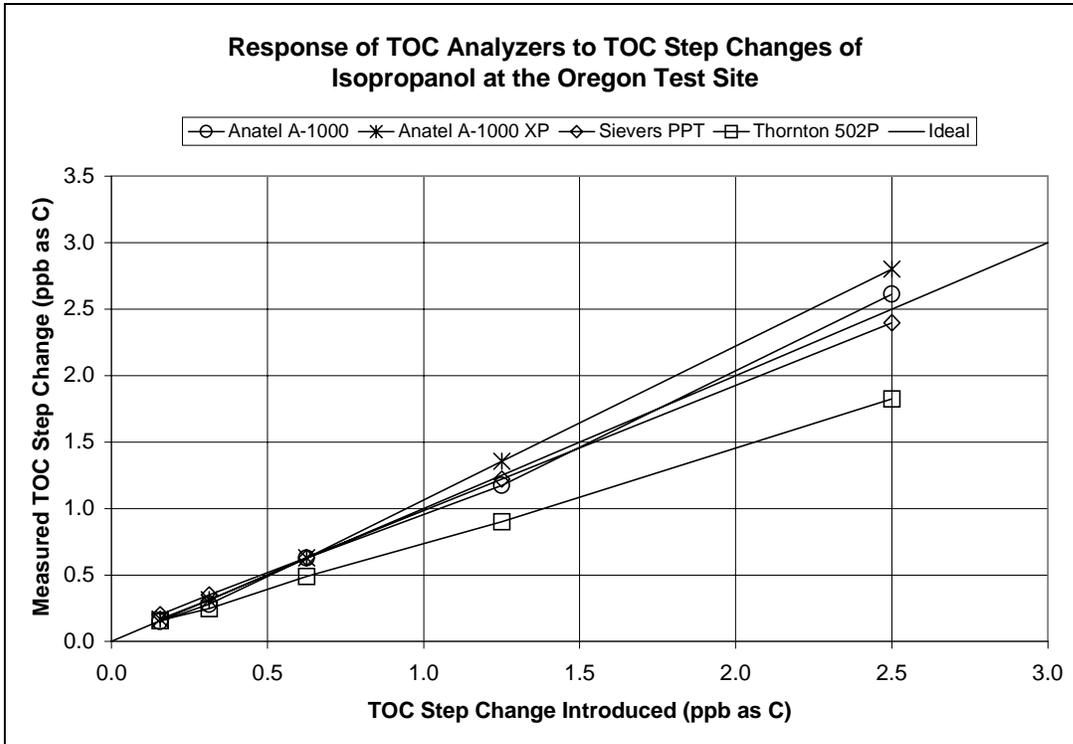


Chart 7: TOC Analyzer Responses to IPA Additions at the Oregon Site.

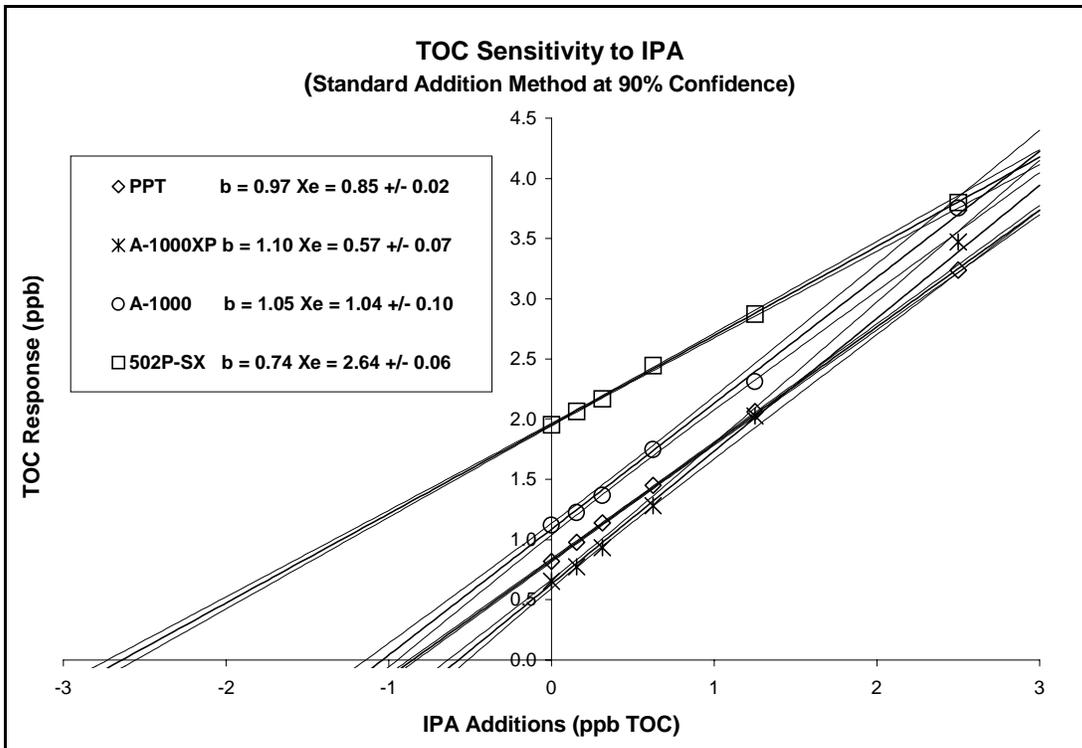


Chart 8: IPA Slope (b), Projected TOC (Xe), and $\pm 90\%$ Confidence Limits on Xe.

The PPT, A-1000XP, and the A-1000 are all within 10% of the correct recovery for IPA. It is unknown why the 502P-SX's recovery was so low on IPA. The algorithm curve for the analyzer was set to "Ultrapure Water". In the manual there is also a curve for "IPA". The response of each analyzer was plotted versus the IPA standard addition concentration in order to fit a least squares line with 90% confidence intervals to the data and is shown in Chart 8. From this fit, the slope and the response corrected level of TOC (Xe) in the UPW were determined for each analyzer. The results of the least squares fit are shown in Chart 8 inside the inserted box. From Chart 8 it can be seen that the PPT's slope is within 3% of the ideal slope which was the best result of all the analyzers. The A-1000 and the A-1000XP have slopes within 10% of the ideal slope. The 502P-SX has a low slope due to its low recovery of IPA. The PPT also has the smallest 90% confidence interval followed by the 502P, the A-1000XP, and the A-1000.

Sodium Benzenesulfonate

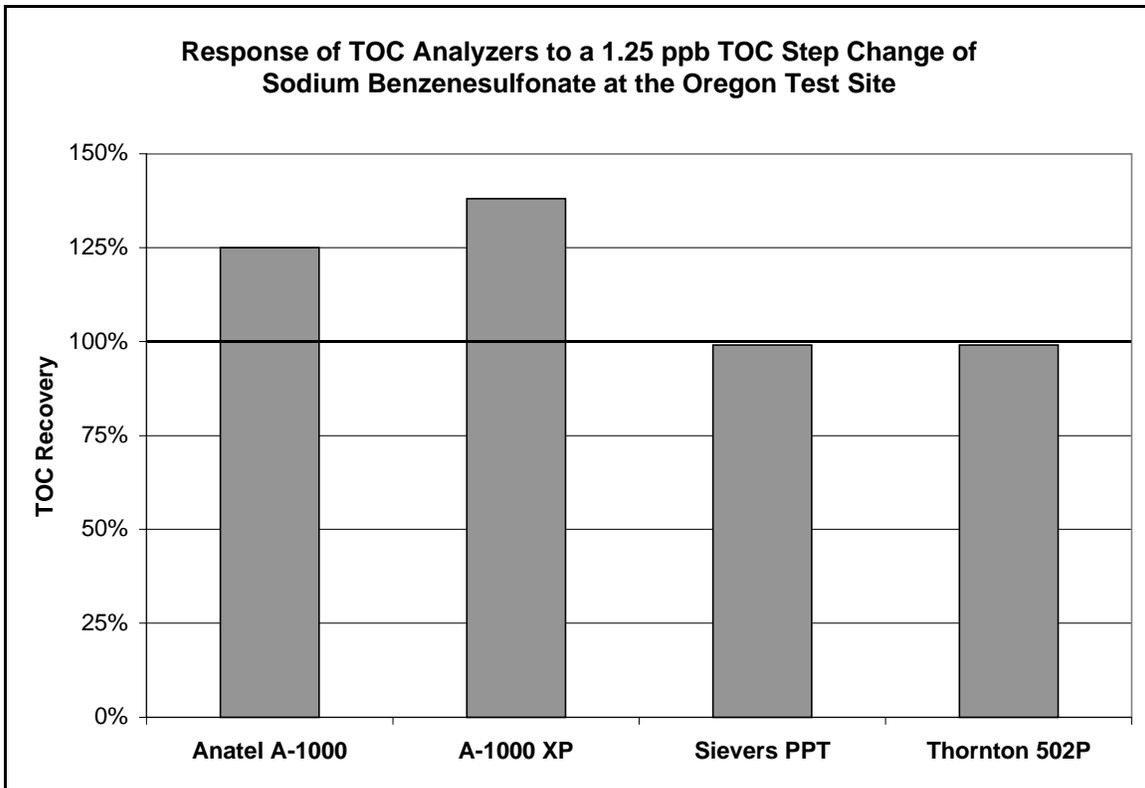


Chart 9: Sodium Benzenesulfonate % Recovery at 1.25 ppb TOC at the Oregon Test Site.

The PPT recovered the benzenesulfonic acid to within 2% of the expected recovery. The high recovery of the A-1000 and the A-1000XP is most likely due to the conductivity increase associated with presence of the SO_4^- ions formed during oxidation. The 502P recovered the benzenesulfonic acid to within 2% of the expected recovery which was unexpected since it should behave similarly to the A-1000XP and the A-1000 with regards to sulfonated hydrocarbons. Its response might be a combination of low recovery (as seen with IPA) and a false positive due to the formation of the SO_4^- ions, resulting in a TOC response close to what was expected.

Glycidol

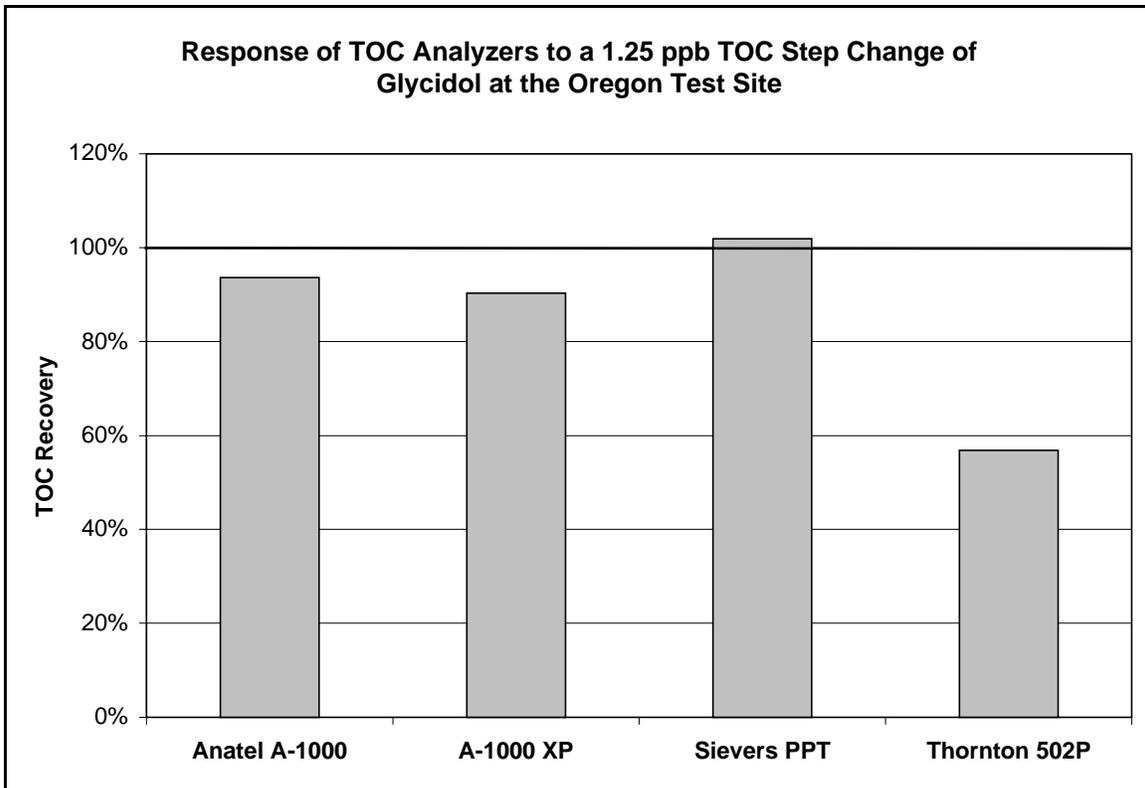


Chart 10: Response of TOC Analyzers to a Step Change of Glycidol at the Oregon Test Site.

Glycidol is an alcohol like IPA so the TOC analyzer's responses to glycidol were expected to be similar to that of IPA. The PPT recovered to within 2% of the correct recovery while the A-1000XP and the A-1000 both recovered the glycidol to within 10%. Again the 502P had a poor recovery of only 57%. The recoveries of the A-1000XP, the A-1000, and the 502P-SX are slightly lower than what they were for IPA which may be because glycidol is harder to oxidize than IPA.

Urea, Trimethylamine, and TMAH

These organic nitrogen compounds are grouped together in charts 11,12, and 14, because of their interesting percent recovery responses with the different TOC analyzers. The most interesting observation in these charts is the very poor recovery of the Anatel A-1000, Anatel A-1000XP, and the Thornton 502P TOC analyzers. The A1000 and the Thornton 502P are responding very much like they did at the Colorado Test Site. The A-1000XP was tested on these compounds for the first time and it is showing better response than the A-1000, but still close to zero recovery. In the TMAH (chart 14) the

same three TOC analyzers actually show a decreasing response as the concentration increases. The effect causes these three analyzers to show a negative percent recovery. Apparently the A-1000XP internally recognized this problem as it produced error #35 on 5ppb TOC of TMAH. The A1000 also reported three error #35's and reported three answers at the same concentration. Error # 35 in both Anatel TOC's is an error for low oxidation rate.

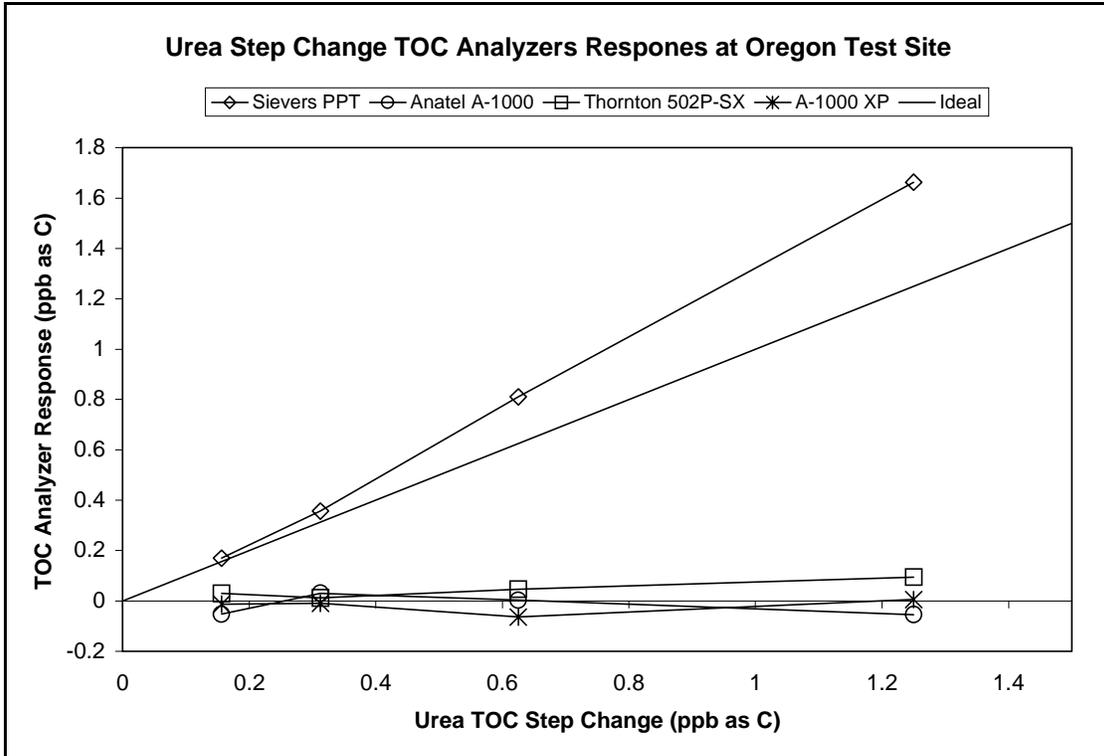


Chart 11: Response of TOC Analyzers to Urea Step Changes

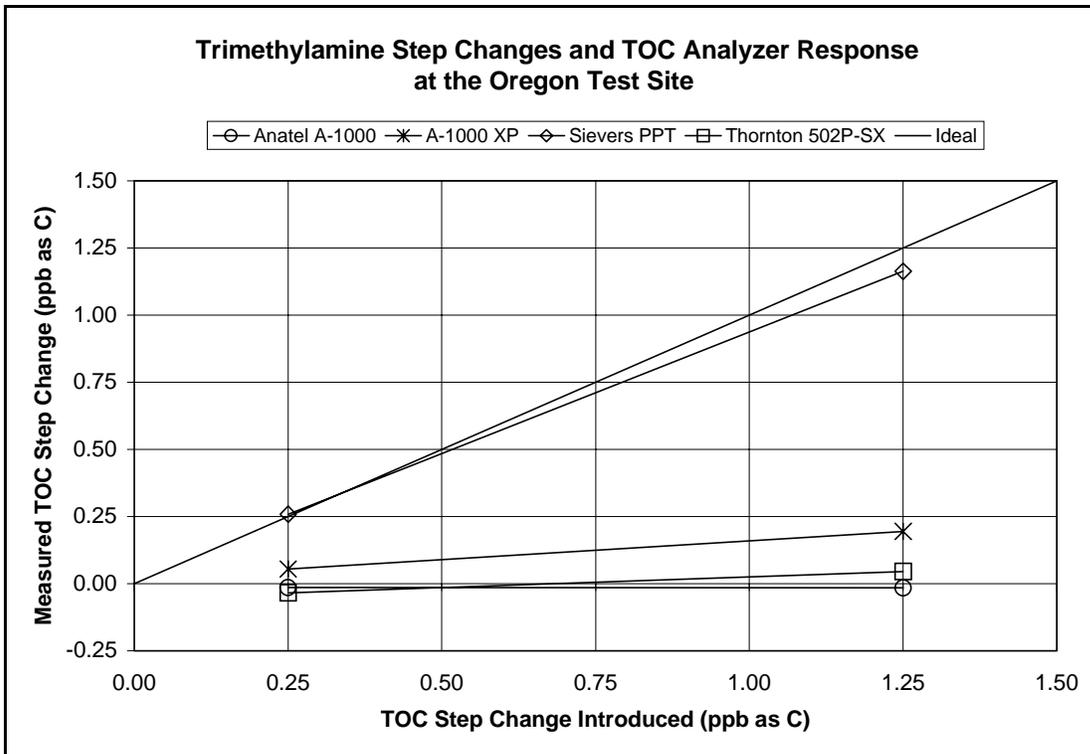


Chart 12: Trimethylamine Step Changes and TOC Analyzer Response

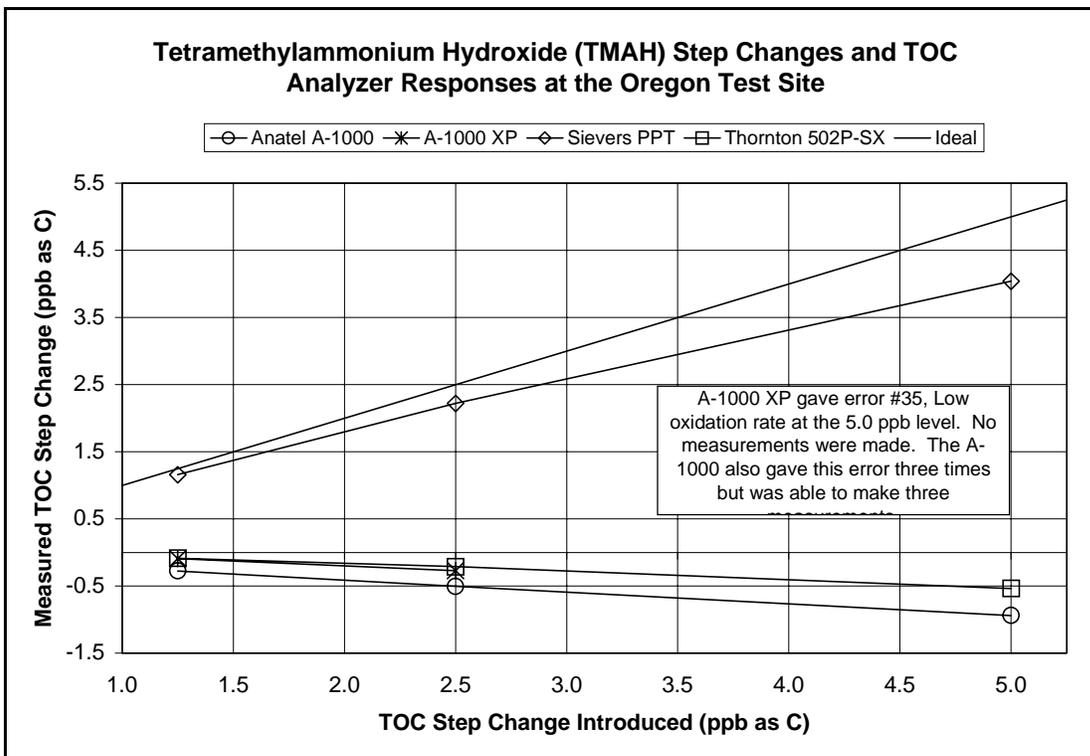


Chart 14: TMAH Step Changes and TOC Analyzer Response

Dichloropropanol

Chart 15 shows the TOC analyzers response to 1,3-Dichloro 2-propanol. This compound was chosen as an analog for chloroform, to simplify the preparation of standards.

Chloroform is found in UPW systems, but it is not easy to prepare as a standard due to its low solubility and high volatility. Both are halogenated organics and are expected to chemically behave the same for the TOC analyzers.

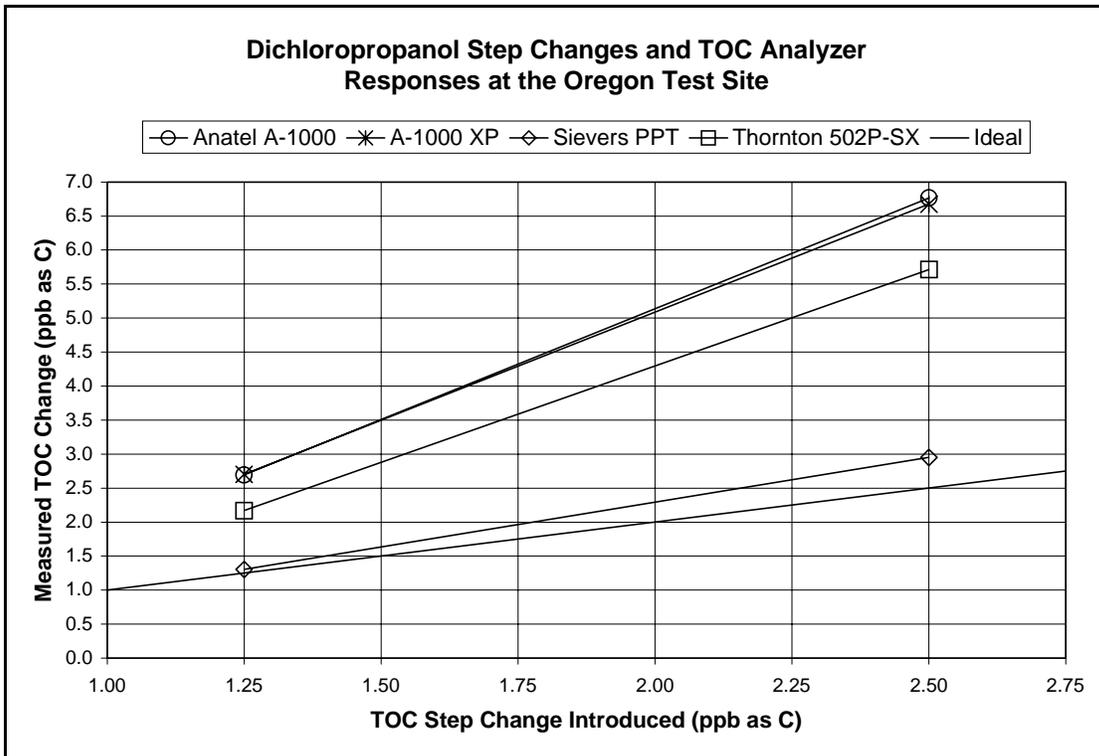


Chart 15: Dichloropropanol Step Changes and TOC Analyzer Responses

The Anatel TOC's show an inflated response to dichloropropanol. Their response is not as large as the chloroform response at the Colorado Test Site. The 502P also shows higher response. These three instruments all measure the CO₂ produced after the UV oxidation with a conductivity sensor. When chlorinated organics are oxidized they produce CO₂ from the carbon atoms and HCl from the chlorine atoms in the organic molecule. The HCl will ionize as a strong acid and be measured by the conductivity sensors in the Anatel TOC's and the Thornton TOC. In these TOC's the extra conductivity from the chloride ion and the hydrogen ion is measured and causes the higher than expected response to TOC. The Ionic Sievers PPT analyzer uses a membrane

to separate the CO₂ from the HCl and only the CO₂ is measured for the TOC and therefore they measure the TOC much more accurately. Other organics that incorporate Cl, Br, N, S, and P in their structure, if they are oxidized completely, are expected to produce the same inflated response in the A-1000, A-1000XP, and the 502P.

Organic Mixtures

Two 1.5 ppb (as Carbon) organic mixtures were run at this test site. They were created from the suggestions of the test site personnel. The results will be reported as bar graphs in charts 16 and 17, due to the single data point step change for each.

Benzenesulfonate, Urea, and Trimethylamine

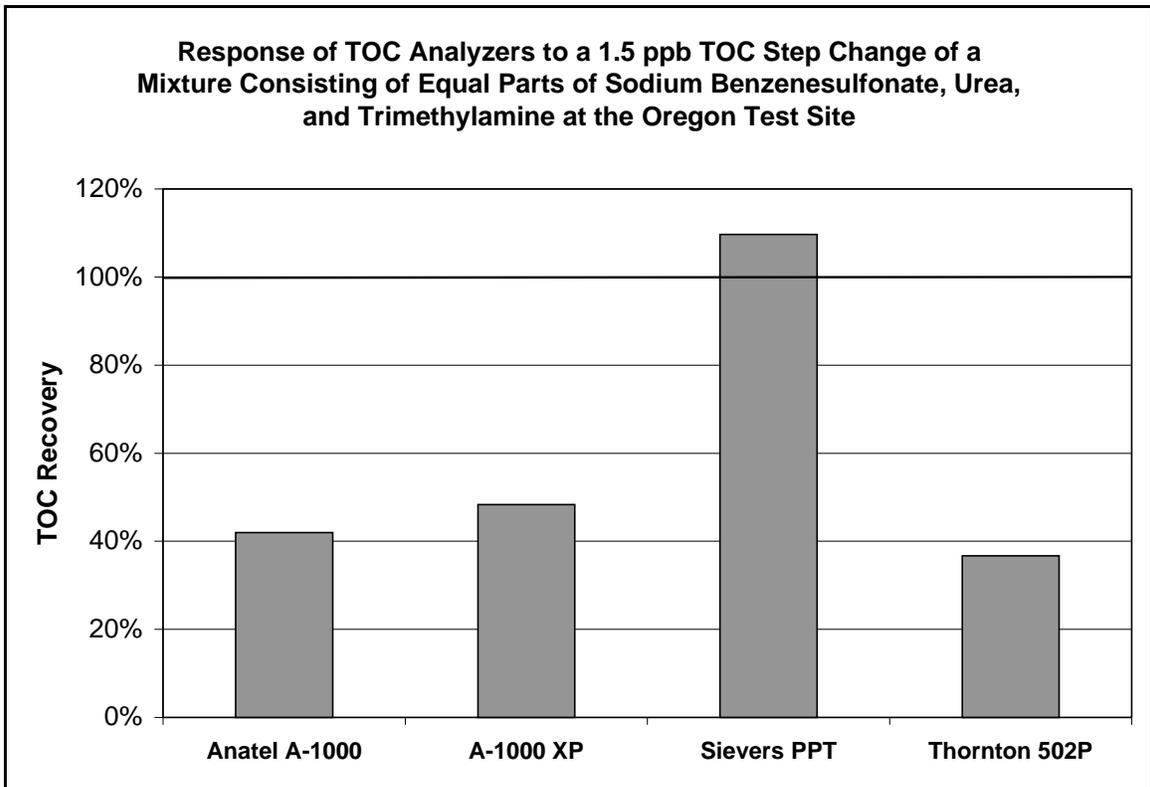


Chart 16: Equal Mixtures of Benzenesulfonate, Urea, and Trimethylamine and the TOC Analyzers Response to a 1.5 ppb as TOC Step Change.

The first mixture prepared consisted of equal parts, measured as TOC, of benzenesulfonate, urea, and trimethylamine. Using the results from the previous standard additions where the mixture’s compounds were run separately, the recoveries of this mixture were estimated for each analyzer. The recovery and estimated recovery of each analyzer are compared in table 6.

Table 6: Recovery and Estimated Recovery of Mixture for Four TOC's

	PPT	A-1000XP	502P-SX	A-1000
% Recovery of Benzenesulfonic Acid /Urea/Trimethylamine Mixture	110%	48%	35%	42%
Estimated % Recovery of Benzenesulfonic Acid/Urea/Trimethylamine Mixture	106%	51%	37%	38%

For each analyzer, the estimated recovery predicted from previous results was within 4% of the actual recovery suggesting that there isn't any interaction between these compounds that affects the TOC measurement of any of the analyzers. The slightly high recovery of the PPT is due to the urea in the mixture which was shown previously to inflate the PPT's recovery. If this mixture is a representative composition of UPW, then Anatel and Thornton instrumentation will only be able to measure between 35 and 50% of the actual TOC compared to the 110% recovery of the PPT.

IPA, Glycidol, and TMAH

This mixture consists of equal parts, on a TOC basis, of isopropyl alcohol, glycidol, and tetramethylammonium hydroxide (TMAH) to simulate compounds in reclaim waters.

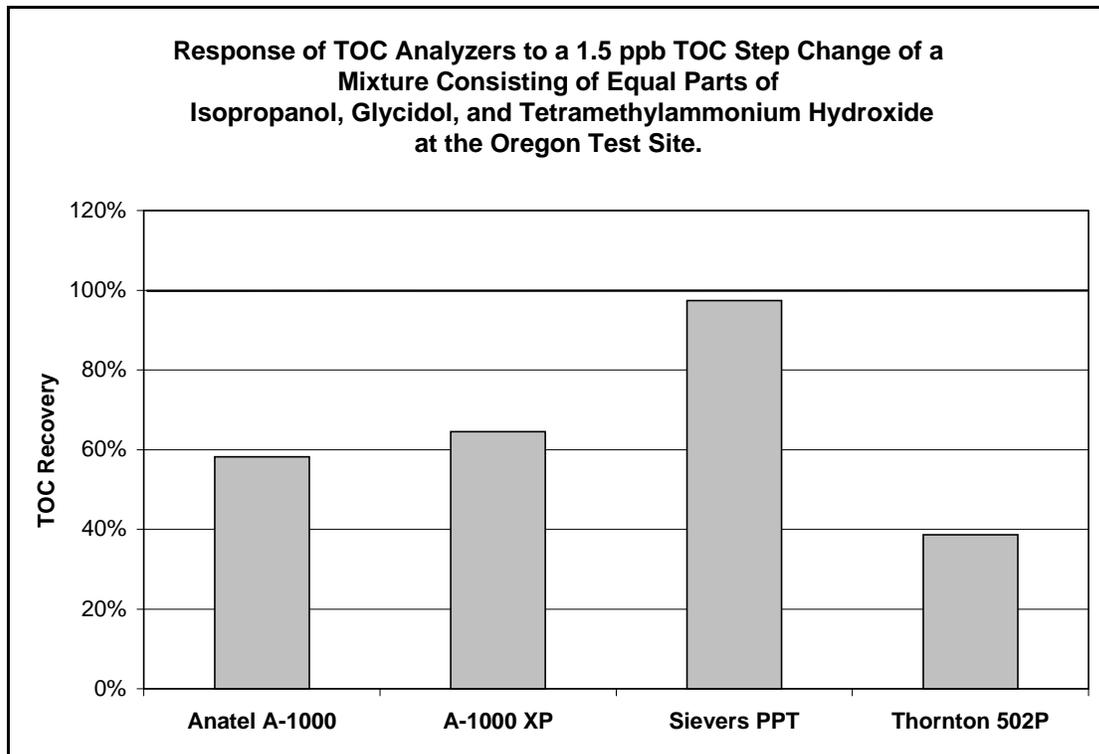


Chart 17: TOC Step Changes of a IPA, Glycidol, and TMAH Mixture.

The results of the standard addition of this mixture are shown in Chart 17. Using the results from the previous standard additions where the mixture's compounds were run separately, the recoveries of this mixture were estimated for each analyzer. The recovery and estimated recovery of each analyzer are compared in table 7.

Table 7. Recovery and Estimated Recovery of a IPA, Glycidol, TMAH standard.

	PPT	A-1000XP	502P-SX	A-1000
% Recovery of IPA/Glycidol /TMAH Mixture	97%	65%	39%	58%
Estimated % Recovery of IPA/Glycidol/TMAH Mixture	99%	63%	43%	57%

For each analyzer, the estimated recovery predicted from previous results was within 4% of the actual recovery suggesting that there isn't any interaction between these compounds that affects the TOC measurement of any of the analyzers. The slightly low recovery of the PPT is due to the TMAH in the mixture, which the PPT was shown previously to not recover completely. If this mixture is a representative composition of UPW with reclaim water, then Anatel and Thornton instrumentation will only be able to measure between 40 and 65% of the actual reclaim water TOC compared to the 97% recovery of the PPT.

TOC Instrument Stability

The stability of each analyzer's TOC measurements was compared using data collected over a twelve hour period. Comparing the stability of these analyzers over such a long period of time was only possible because of the high stability of this test site's UPW system. The Thornton 502P-SX was not included because it did not have a printer, the data was collected overnight, and there was no obvious way to retrieve the data from it. The data collected from the two PPTs, the A-1000XP, and the A-1000 was plotted and the results are shown in Chart 18. The two PPT's tracked each other almost perfectly while the A-1000XP and the A-1000 showed no similarities, the A-1000XP measuring half the TOC of the A-1000. The A-1000XP is significantly more stable than it's predecessor the A-1000 at low levels of TOC.

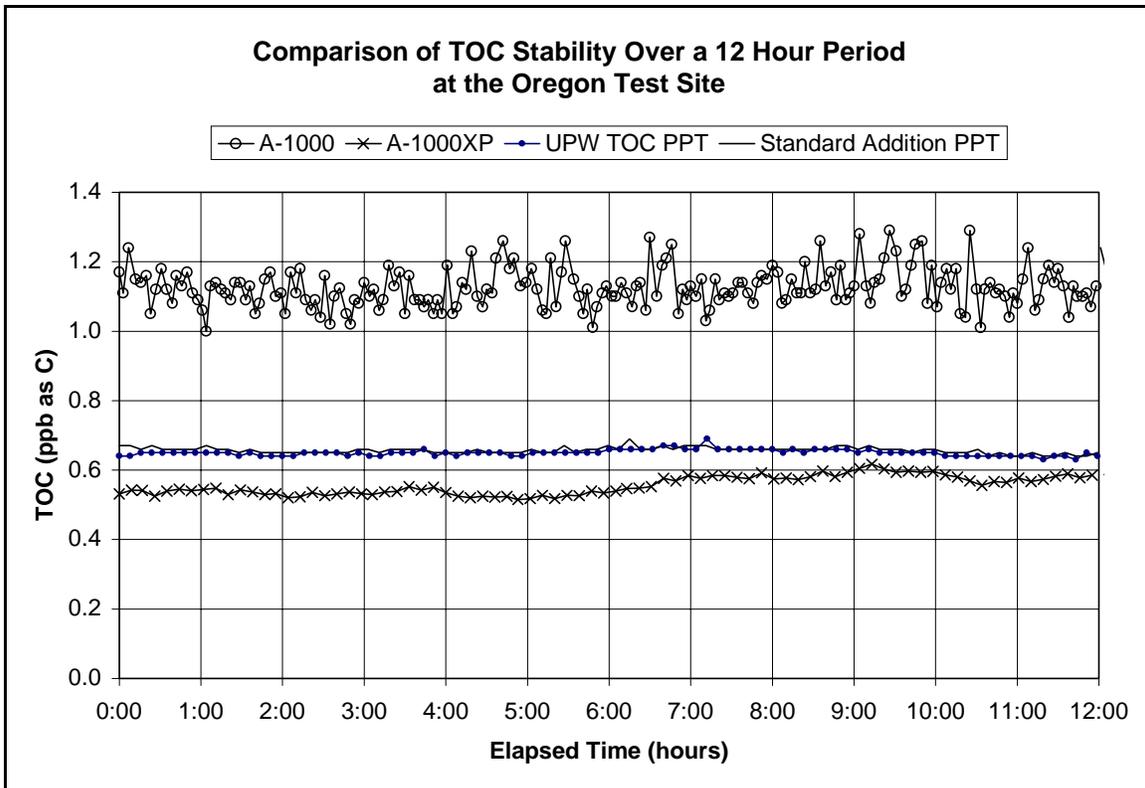


Chart 18: TOC Measurements on UPW at the Oregon Study Site.

The average TOC measurement and the standard deviation of the TOC measurements for each analyzer are shown in table 8.

Table 8. Average and Standard Deviation of TOC Measurements Made Over a Twelve Hour Period.

	PPT #1	PPT #2	A-1000XP	A-1000
Average (ppb)	0.650	0.657	0.555	1.12
Standard Deviation (ppb)	0.009	0.009	0.027	0.06

The stability and precision on the 12 hour overnight run shows the A-1000XP standard deviation (± 0.027 ppb) is much lower than that of the A-1000 (± 0.06 ppb). During the same test the Ionics Sievers PPT standard deviation (± 0.009 ppb) is one third of the A-1000XP standard deviation (± 0.027 ppb). The PPT standard deviation was two times higher during the IPA injections (± 0.02 ppb) compared to the 12 hour blank run PPT standard deviation of (± 0.009 ppb), suggesting the addition device was adding about

± 0.01 PPB noise. Additional support for this statement follows from data showing the reference PPT standard deviation during the IPA additions was ± 0.01 ppb, this also suggests the dilution device was contributing the difference of about ± 0.01 PPB.

A summary of the chemical additions to the UPW at the Oregon test site is shown in Chart 19.

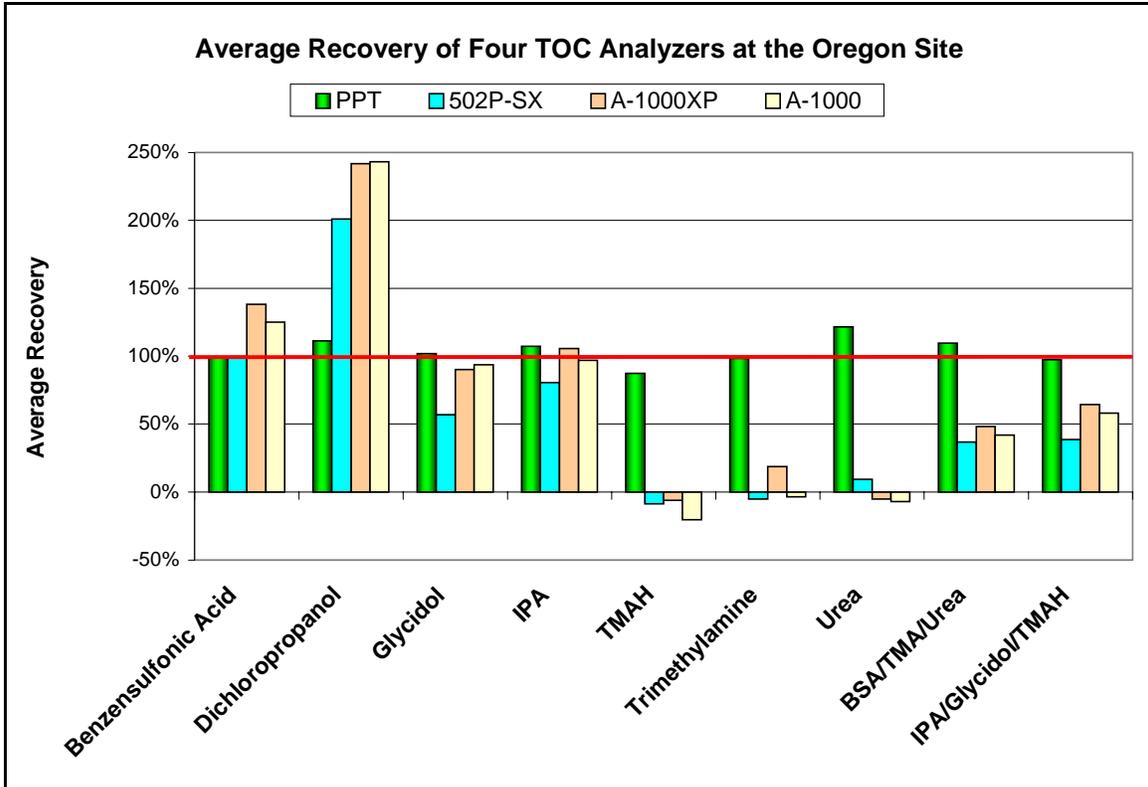


Chart 19: Overview of TOC Responses for all Compounds Tested at the Oregon Test Site.

The data collected from this site shows the problem with organic nitrogen compound recoveries for the A-1000, A-1000XP, and the Thornton 502P. This study repeats the results from the Colorado test site for urea, but it is clear the recovery problem extends to two other organic nitrogen compounds, trimethylamine and TMAH. The results from the TOC analysis of dichloropropanol at this site show a high percent response from the A-1000, A-1000XP, and the Thornton 502P. This effect has been known since 1989 (10). The dichloropropanol compound shows the same higher response from these three TOC analyzers in the same way they showed higher recovery at the Colorado test site when

testing chloroform. The Thornton 502P is showing higher response to IPA at the Oregon test site (74%) than at the Colorado test site (42%). It is not know why this is so. The A-1000 is showing about the same recovery for IPA at both sites.

Test Site: Japan

The Japanese Test Site personnel made the decision to test three different TOC analyzers on four different organic compounds. The analyzers selected by the test site personnel were all reagentless TOC's and included the Anatel A-1000, Anatel A-1000XP and the Ionics Sievers PPT. The compounds and the concentrations tested are shown in Table 9. At this site we ran many multiple runs of the same standard concentrations. Multiple runs are reported in Table 9, in parentheses after each concentration.

Table 9: Compounds Studied at the Japanese Site

Compound	Concentration (ppb as C) and replicates (#X)
Isopropyl Alcohol (IPA)	0.25, 0.3, 0.35, 0.625, 1.25 (3X), 2.5 (2X)
Urea	0.35, 0.625, 1.25 (2X), 2.5
Tetramethylammonium Hydroxide (TMAH)	0.25, 0.35, 0.625, 1.25 (2X)
1,3-Dichloro-2-propanol (DCP)	0.35, 1.25

The analyzers were setup according to the schematic shown in Figure 4.

The UPW system used in these experiments contained high concentrations of oxygen. The system pressure was approximately 20-psi. This was the maximum pressure that could be attained. The sample coming from the UPW system was passed through a pressure regulator prior to entry into the standard addition device. This reduced the inlet pressure to 15-psi in order to meet the operating specifications of the standard addition apparatus.

The standard addition device utilized a digital flowmeter to measure the flow rate of the bulk ultrapure water stream. Based on this measured flow rate and the concentration of the total organic carbon standard to be introduced, the apparatus automatically calculated

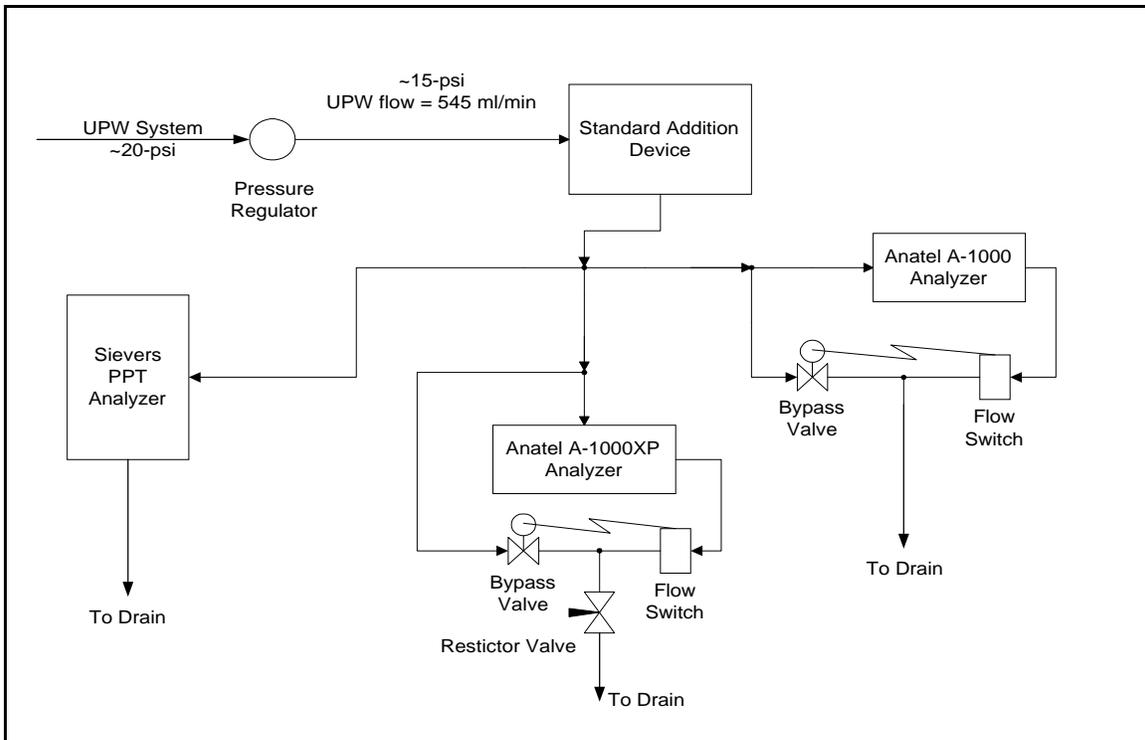


Figure 4: Apparatus Setup at the Japanese Test Site

the dilution ratio necessary to generate a discreet TOC step change in the system. The device then used a syringe injection system to carry out this dilution. The accuracy of the flowmeter was verified at the test site by manually measuring the outlet flow rate from all three analyzers. It was found that the measured flow rate was about 545 ml/min. This measured value was within 0.3% of the value displayed on the flowmeter. The syringe used to introduce the TOC standards was validated at Sievers and was found to be accurate to within 1%.

The PPT had a UV lamp that was just nine days old. The PPT was set up to run in “ANALYSIS” mode. The outlet flow rate from this analyzer was approximately 130 ml/min.

The A-1000 and the A-1000 XP were both supplied by the test site personnel for these experiments. The status of the UV lamps in the two instruments was unknown. Both instruments were installed in the vertical position so that the front panel displays faced upward. This was the manufacturer’s recommended operating configuration. A bypass loop was attached to each of the instruments. These loops were designed to limit the change in sample flow that occurred when the internal valve within the two Anatels

opened and closed during analysis. Through careful adjustment of a needle valve connected to each of the bypass valves, we were able to make the flow rates through the bypass loops equal to the flow rates through the Anatel analyzers. This helped make the overall flow rate constant and minimized the impact of pressure variations on other analyzers and on the standard addition device. A needle valve was also attached to the outlet from the A-1000 XP analyzer. This valve was used to force the flow through the PPT to a value greater than 100 ml/min (the minimum operating specification for the PPT).

Experimental Procedure

The concentration of each of the test standards was verified at Sievers using a Sievers Model 800 analyzer. All standards were verified to be within 0.4% of the expected value. Eight pre-cleaned polysulfone vials (two for each compound) were then filled with the standards, sealed with caps and septa, and shipped to the test site in Japan.

Prior to beginning injections, the two Anatels were switched to “AUTO TOC” mode. The sample time was set to six minutes and the cycle time was set to eight minutes. The “VALVE @ IDLE” state was set to the OPEN position. All three analyzers were allowed to collect data for approximately two hours before injections began. The data was collected using three printers attached to the three instruments. The syringe on the standard addition device was flushed with UPW three times to clean out any residual contamination.

Before the standard additions were started the two Anatel analyzers were rinsed down in the “CLEAN” mode and the PPT was rinsed down in the “ANALYSIS” mode overnight. On the second day, the standard addition tests were started.

Isopropanol (IPA), Urea, TMAH, Dichloropropanol

The results of the standard injections are shown in charts 20-25.

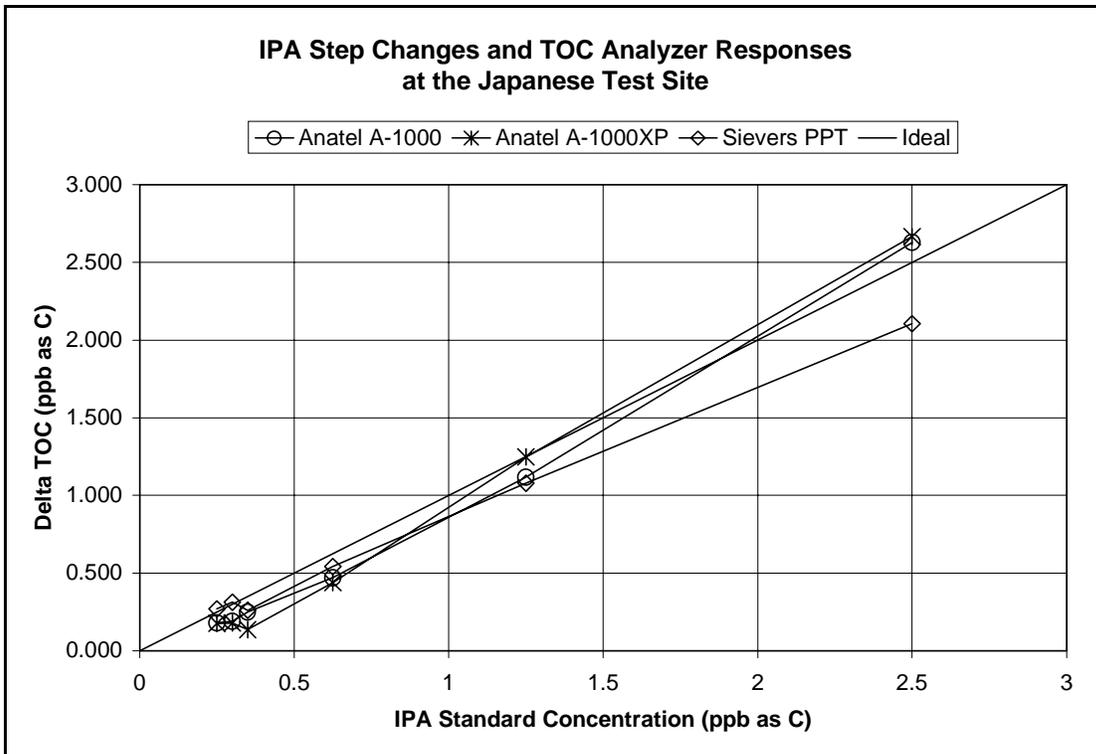


Chart 20: IPA Step Changes and TOC Responses at the Japanese Test Site.

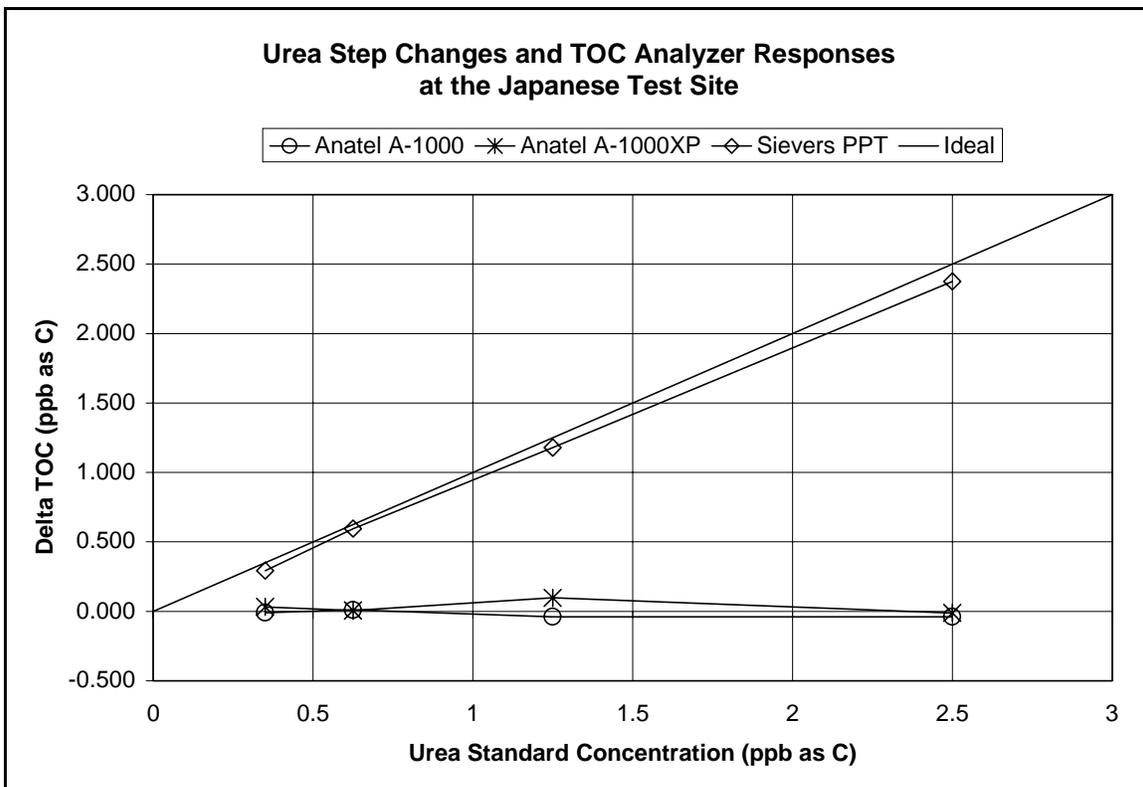


Chart 21: Urea Step Changes and TOC Responses in Japan.

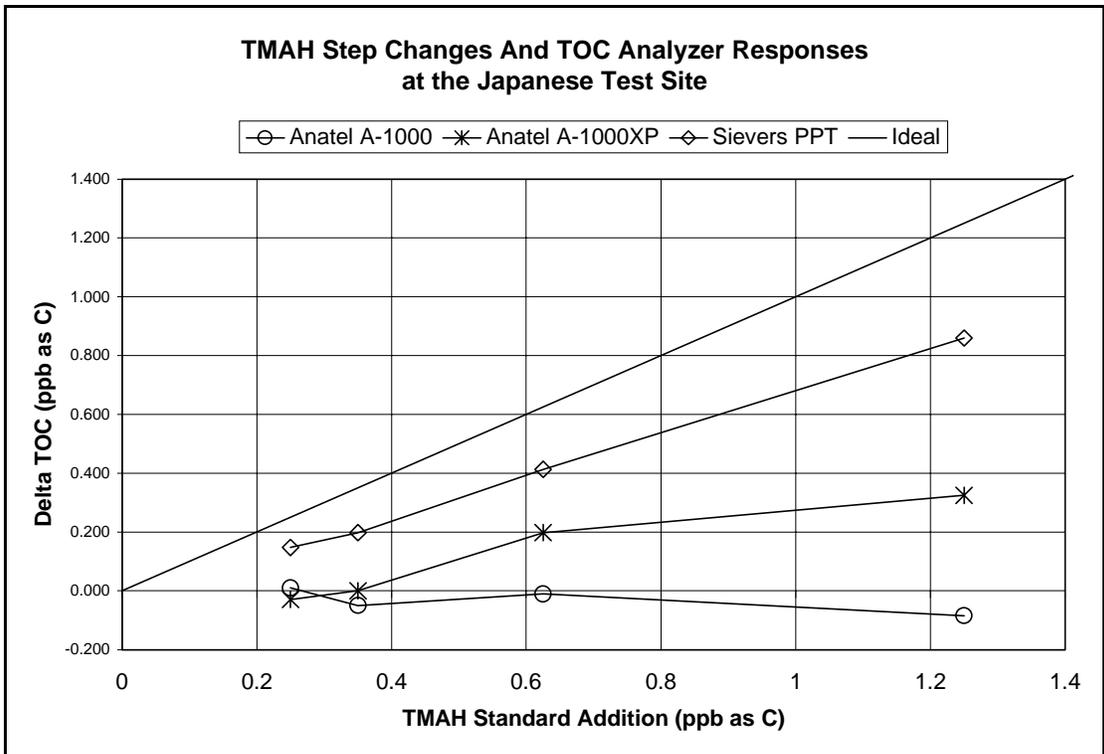


Chart 22: TMAH step changes and TOC Responses at the Japanese Test Site.

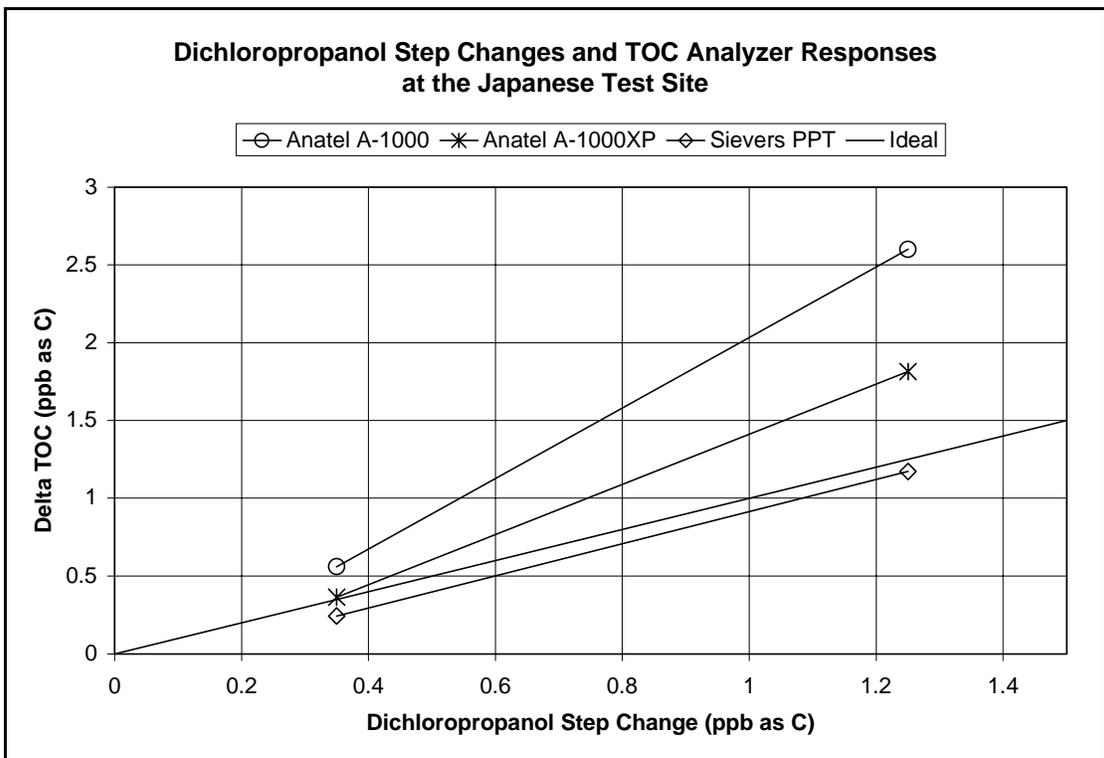


Chart 23: Dichloropropanol Step Changes and Responses at the Japanese Test Site.

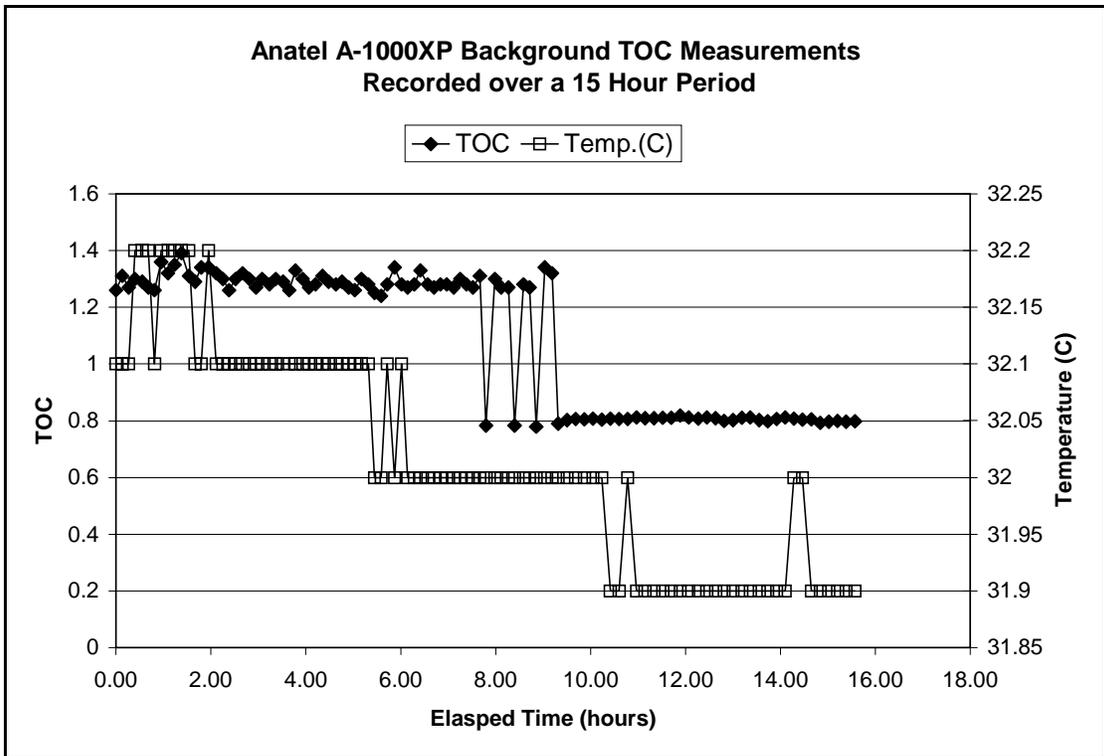


Chart 24: A-1000XP Switching between XP and A1000 Mode at 32 °C.

Review of chart 20 shows all the analyzers had similar response recoveries to the IPA injections at 1.25 ppb and lower. At 2.5 ppb the Sievers PPT recovery was about 89% and was lower than the other TOC analyzers, however the response increased as the concentrations decreased. The standards average deviations for all the IPA injections are shown in Table 10. The higher average standard deviation for the A-1000XP on IPA injections is probably due to the thermal related operating mode changes.

Table 10: Average Standard Deviations on IPA Additions at the Japanese Test Site

Analyzer	Standard Deviation (ppb as C)
Sievers PPT	± 0.065 ppb
Anatel A-1000	± 0.189 ppb
Anatel A-1000XP	± 0.199 ppb

The air and UPW temperature averaged about 32 °C at this site. This caused problems for the A-1000XP, as it would switch between XP analysis mode and standard A1000 analysis mode. This shift was indicated on the TOC output by a 0.5 ppb change and this often resulted in higher standard deviations for measurements. Chart 24 shows the step

change at 32°C in the TOC results due to the switch between the XP and normal A1000 analysis modes.

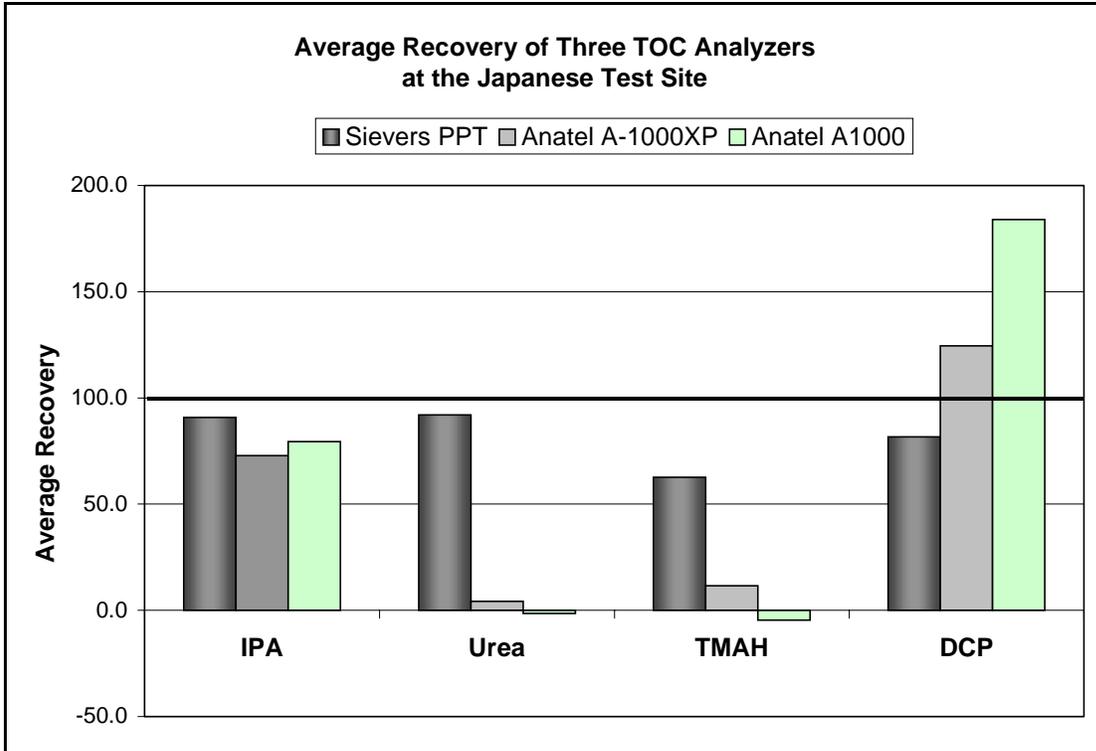


Chart 25: Overview of Average Responses for all Compounds at the Japanese Site.

Chart 25 summarizes shows the average percent recovery response for all compounds for each instrument. In all cases the average response is closer to 100% for the Sievers PPT than either of the Anatel TOCs. It is not known why all the analyzers reported lower recovery on IPA, Urea, TMAH, and DCP than in the prior experiments (Charts 6 and 19). As shown in the prior two test sites the Anatels both showed almost no response to urea and TMAH. The Anatels also showed a much higher response than the PPT to the dichloropropanol, which also repeats the results from the prior Oregon test site.

Test Site: Korea

At this site we tested four compounds, one mixture, and two different TOC analyzers. The analyzers tested were the Ionics Sievers PPT and the Anatel A-1000XP. The dissolved oxygen level in the UPW, at this site, averaged 0.34 ppb. The compounds tested and the test concentrations are shown in Table 11.

Table 11: Compounds Tested at the Korean Site.

Compounds Tested	Test Concentrations (ppb as Carbon)
IPA	0.25, 0.625, 1.25
Sucrose	0.25, 0.625, 1.25
Trimethylamine (TMA)	0.25, 0.625, 1.25
Dichloropropanol (DCP)	0.25, 0.625, 1.25, 5.0
IPA / TMA / DCP	0.25, 0.625, 1.25

The IPA, TMA, and DCP mixture was made up at a ratio (as TOC) of 31.9%, 32.5%, and 35.6% respectively. The arrangement of the TOC analyzers and the standard addition system is shown in Figure 5. All sample lines are ¼" OD Teflon tubing. A pressure regulator (not shown in Figure 5) was used to regulate the pressure to 20 psig. The A-1000XP's sample time was set to three minutes and its *Valve@Idle* setting was set to "Open" to permit continuous flow through the instrument. Consequently, the bypass loop (as shown in Figure 5) on the A-1000XP was not required.

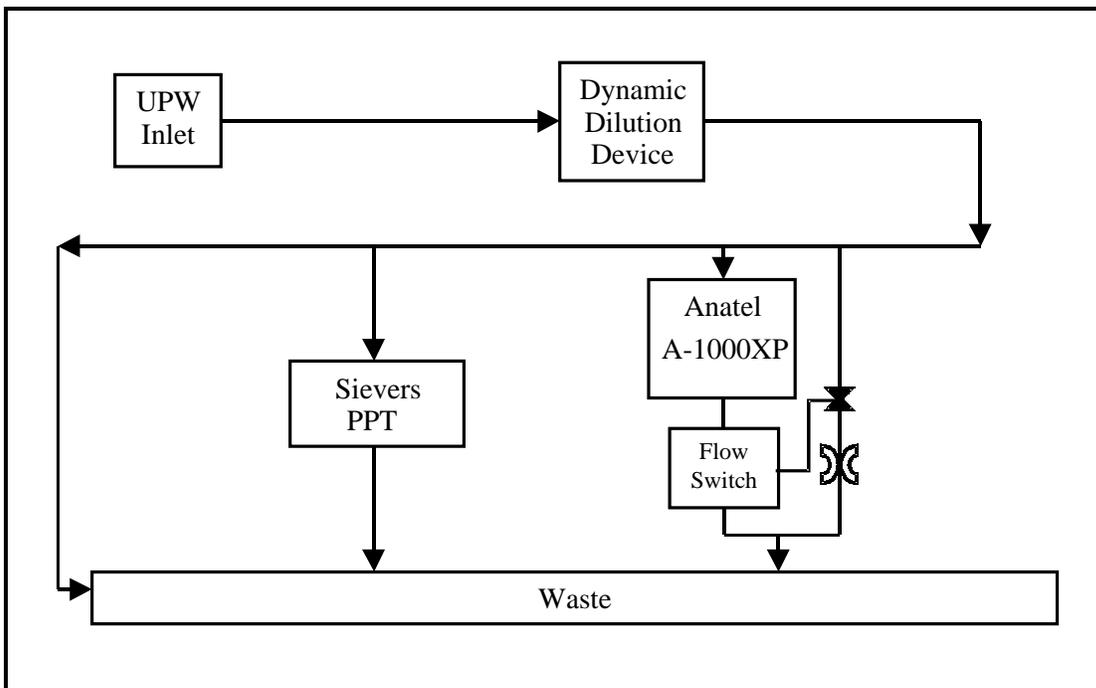


Figure 5: Apparatus Setup at the Korean Test Site.

The experimental procedure used at the Japanese test site was used at this site. The results of the standard injection experiments follow in Charts 26-31.

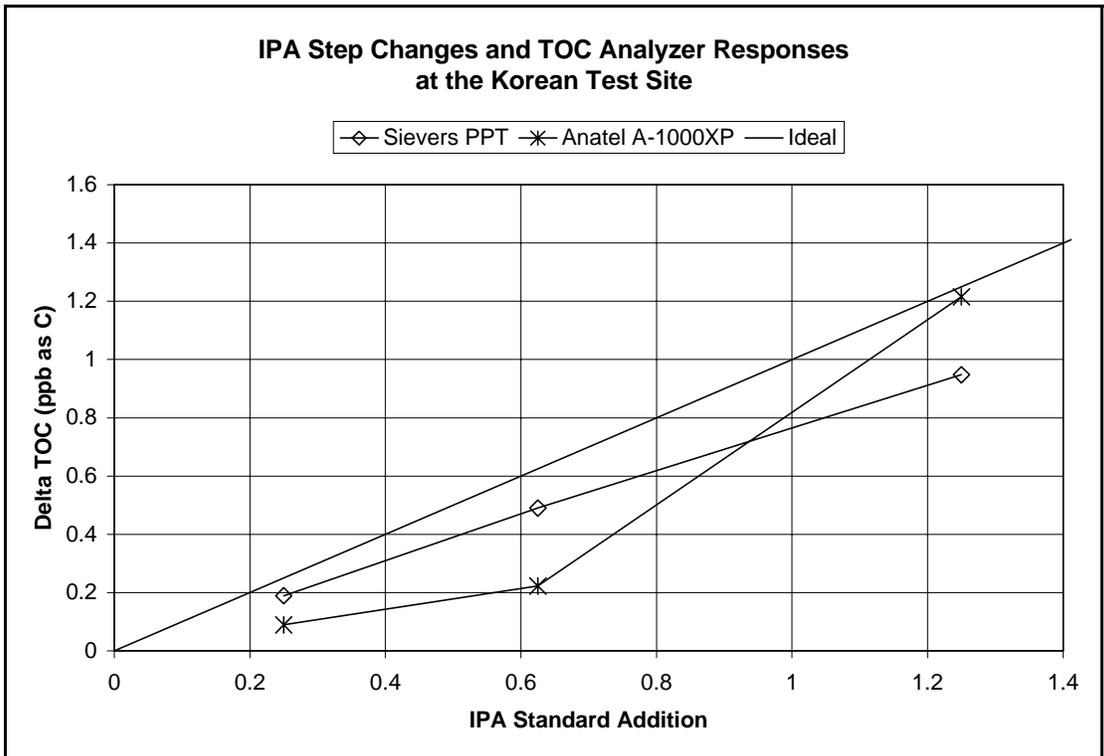


Chart 26: IPA Step Changes and TOC Responses at the Korean Test Site.

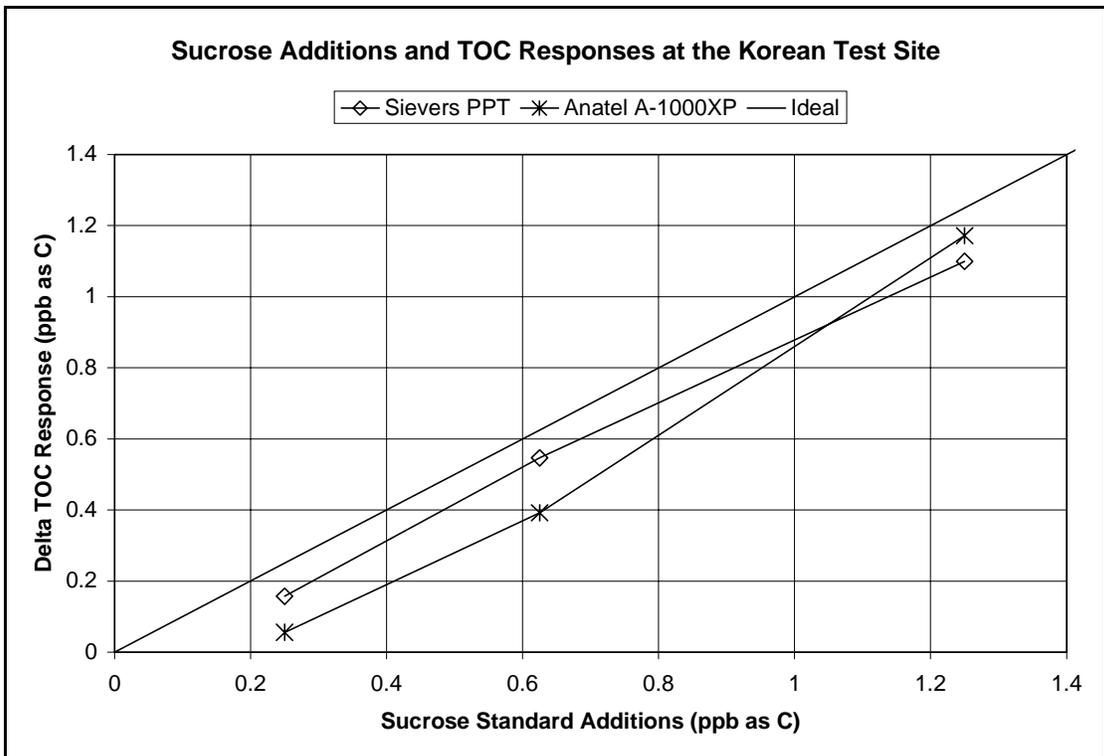


Chart 27: Sucrose Standard Additions and TOC Responses at the Korean Test Site.

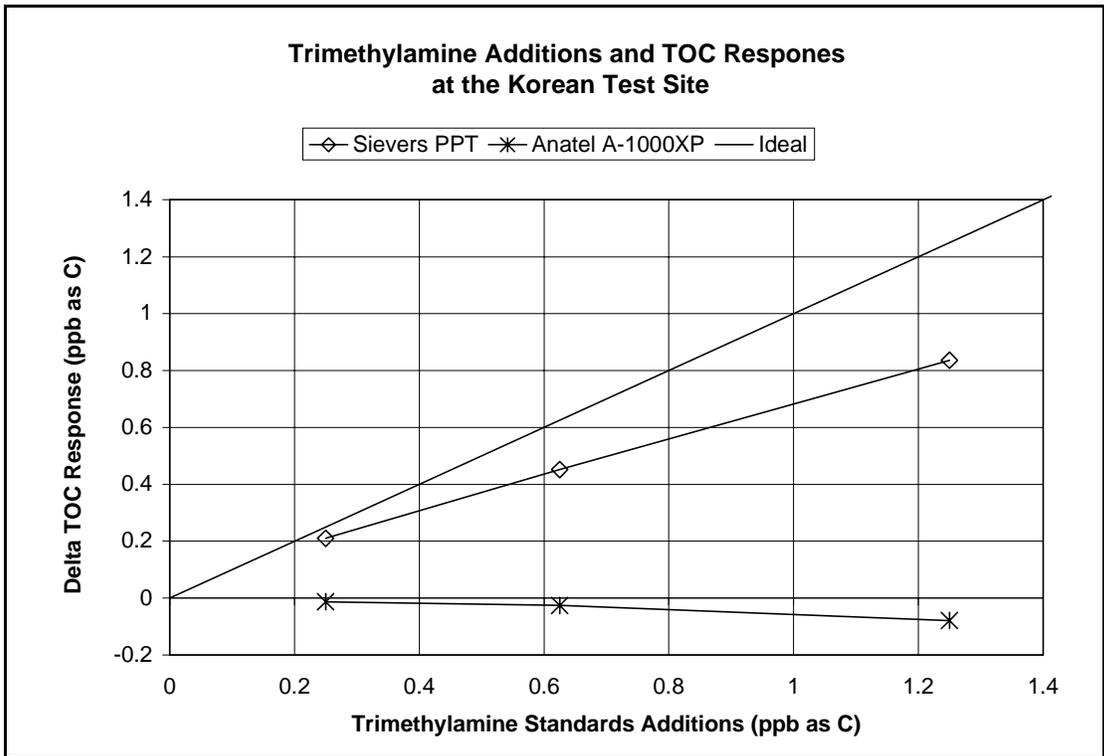


Chart 28: Trimethylamine Additions and TOC Response at the Korean Test Site.

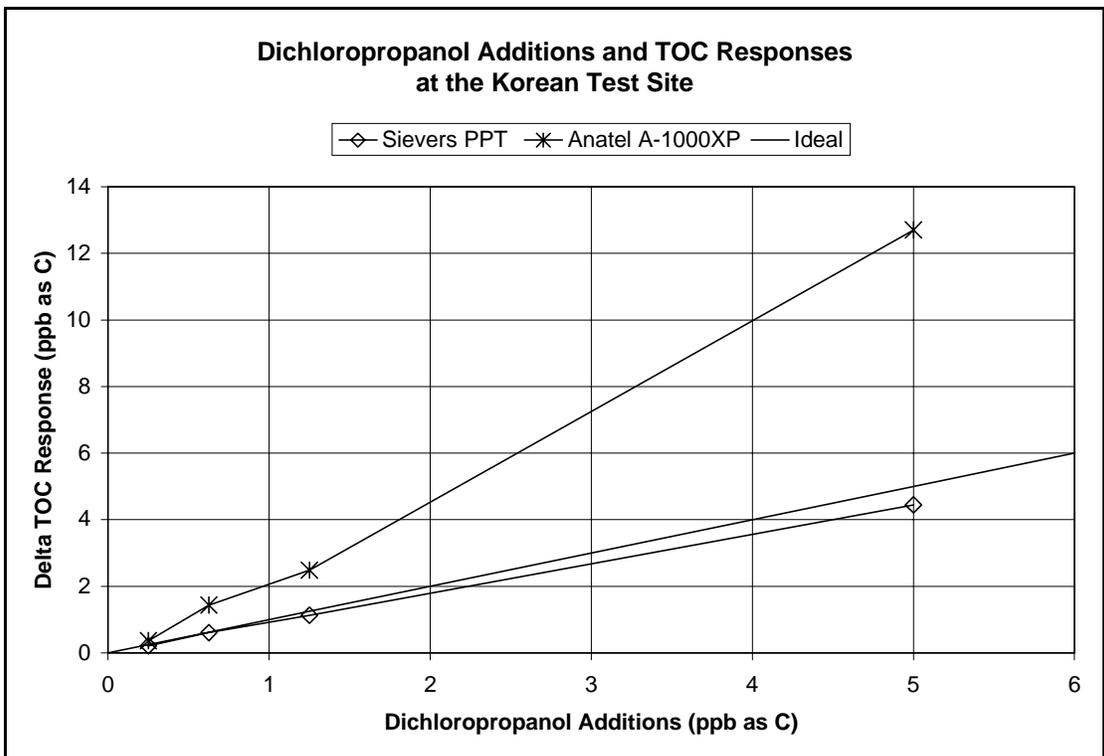


Chart 29: Dichloropropanol Additions and TOC Responses at the Korean Test Site.

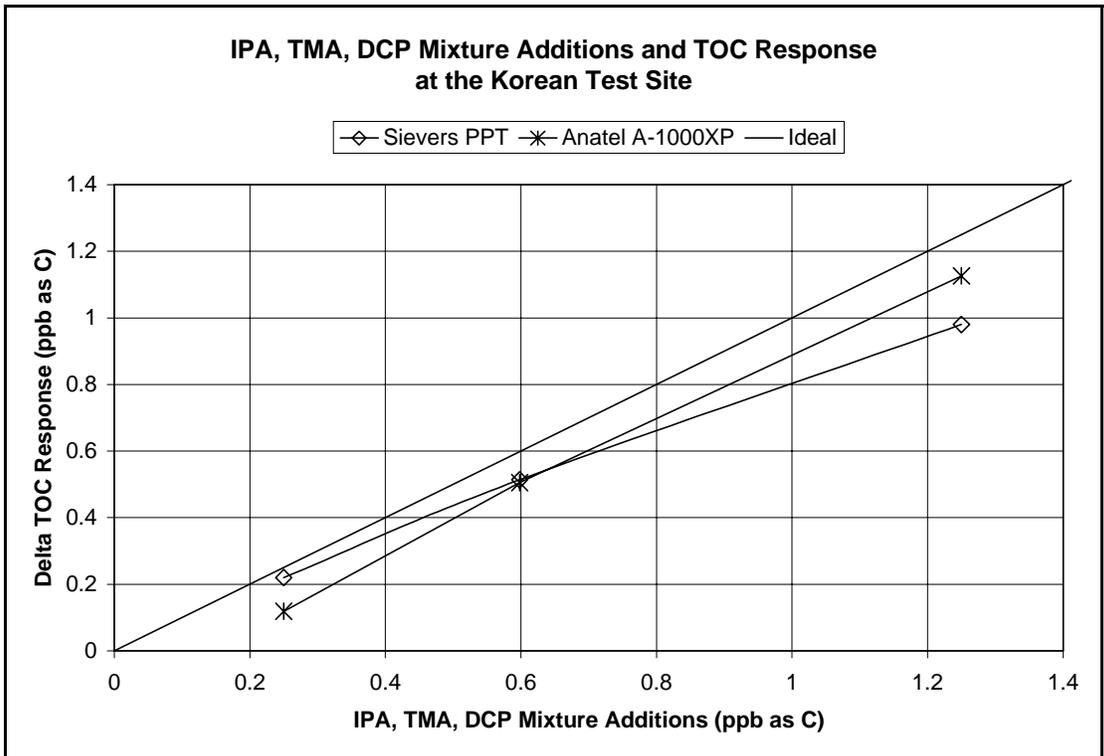


Chart 30: IPA, TMA, DCP Mixture and TOC Response at the Korean Test Site.

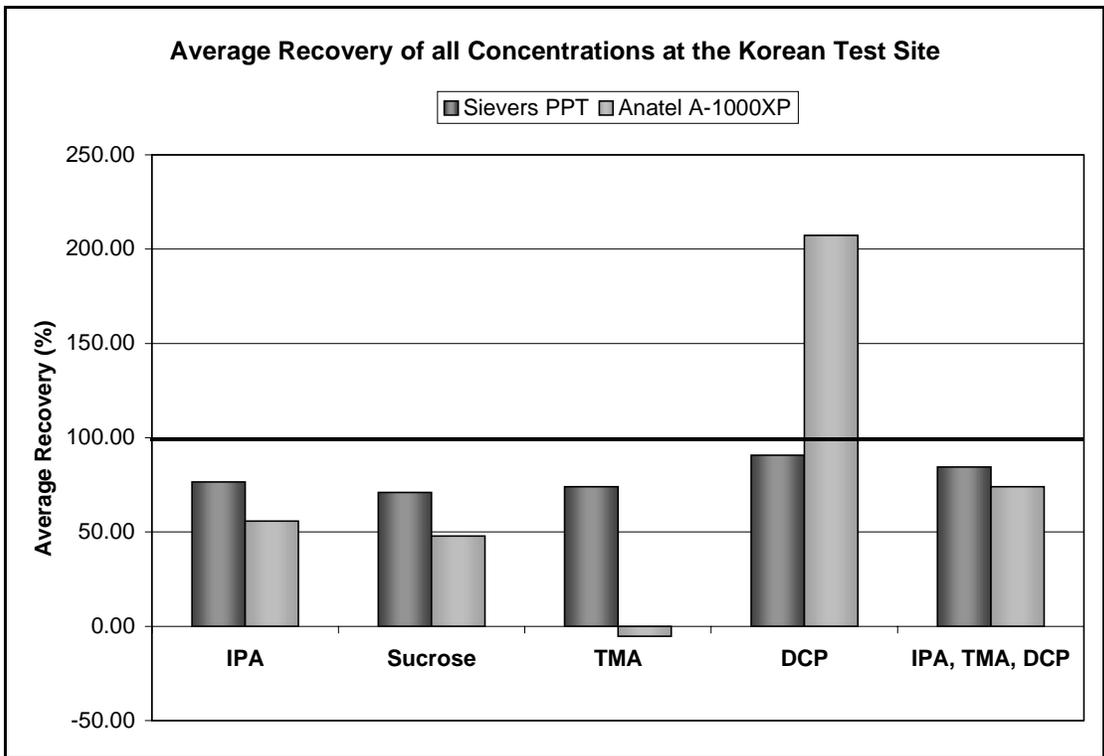


Chart 31: Average TOC Recovery of all Concentrations at the Korean Test Site.

A review of charts 26-31 show the overall same result as in the prior site testing. The response to the all compounds is slightly lower on both TOC analyzers than for equivalent testing at the Colorado and the Oregon test sites. Chart 31 shows a plot of the average recovery of all the different concentration runs on each compound. As in the prior testing the PPT has an average recovery closest to 100% for all compounds. It is interesting that the mixture solution is made up of a compound that the A-1000XP does not see (TMA), one compound that it measures much to high (dichloropropanol), and a third compound it recovers very well (IPA). This results in an almost correct measurement for the A-1000XP. Since the expected TOC results to a compound mixture can be predicted by the individual responses for each compound, it is possible to prepare mixtures that will produce correct TOC recoveries for the Anatel A-1000, A-1000XP, and the Thornton 502P if the mixture contains compounds that are individually over or under recovered.

Test Site: Arizona, USA

This semiconductor manufacturing site injects hydrogen gas into their UPW to react with dissolved oxygen in the presence of a palladium catalyst which converts the dissolved oxygen and hydrogen into water. The resulting dissolved oxygen concentration is typically below 5 ppb depending on the amount of hydrogen used and the incoming dissolved oxygen concentration. Some residual hydrogen remains in the UPW and is present when the water reaches the analytical loop where the TOC of the UPW is measured. Almost all semiconductor manufactures use a reagentless TOC analyzer to analyze the TOC of their UPW. These analyzers use ultraviolet radiation to oxidize organic compounds and measure the conductivity change of the UPW. Without dissolved H₂ in the water the UV reactor normally converts the organics to CO₂ which is then measured by one of a couple of different methods. Dissolved hydrogen can act as a reducing agent and interfere with the oxidation process, resulting in little or no production of CO₂. The lack of CO₂ formation from the organics produces little or no conductivity change and small or no TOC measurement in the analyzers that measure for CO₂ using conductivity such as the 502P or the A-1000. The lack of CO₂ was expected

to cause the PPT, which measures CO₂ selectively through a membrane, to read low as well. It is possible to produce ionic organic acids from organics in a reducing reactor environment, but it is not known if this type of reaction will produce a quantifiable TOC result.

The compounds and concentrations tested at this site are shown in Table 12.

Table 12: Compounds Studied at the Arizona Test Site

Compounds	Concentrations (ppb)
IPA and dissolved H ₂	IPA = 5.0 ppb as C Dissolved H ₂ = 67 ppb as H ₂
IPA and dissolved H ₂	IPA = 5.0 ppb as C Dissolved H ₂ = 84 ppb as H ₂
Urea and dissolved H ₂	Urea = 5.0 ppb as C Dissolved H ₂ = 69 ppb as H ₂
Urea and dissolved H ₂	Urea = 5.0 ppb as C Dissolved H ₂ = 84 ppb as H ₂

The site managers decided to study the response of four TOC analyzers to 5.0 ppb TOC step changes of IPA or urea at two different levels of dissolved hydrogen. Three of the TOC analyzers were reagentless, the Anatel A-1000, the Thornton 502P-SX, and the Sievers PPT, and one TOC analyzer used an oxidizer reagent, the Sievers 800.

PPT serial number 9809-0006 and PPT serial number 9901-0018 had UV lamps that are nine months old and five months old respectively out of an expected lifetime of 12 months. The 800 had a UV lamp that was three months old out of an expected lifetime of six months and both reagents were two months old out of the expected lifetime of three months. The 800 had been prepared for low TOC measurements by setting both the acid and oxidizer flow rates to 0.5 µL/minute and correcting the “TC Zero Offset” for the TOC contributions from each reagent. Setting the oxidizer flow rate to 0.5 µL/minute was expected to ensure complete oxidation of organic compounds without sensitivity to dissolved hydrogen concentrations. The A-1000 was supplied by the site personnel and had been calibrated 5 months prior to this experiment. It is presumed that the UV Lamp

was replaced at the time of the calibration. The 502P-SX was a loaner/demo unit that was supplied to the site for evaluation. The usage time of the 502P UV lamp was unknown. The apparatus layout is shown in Figure 6.

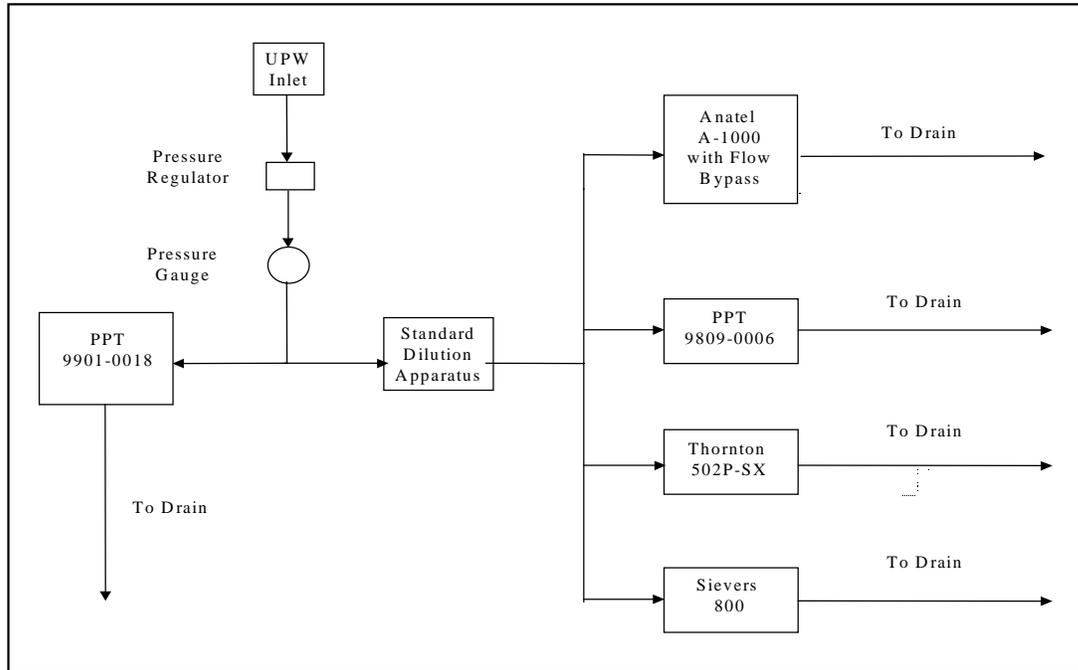


Figure 6: Equipment Setup at the Arizona Test Site.

Referring to Figure 6, the inlet lines to the standard dilution apparatus and to each of the five instruments were 1/4" O.D. 316L stainless steel that had been cleaned by the manufacturer and been flushed with UPW at Sievers overnight. Stainless steel was used to prevent the diffusion of oxygen into the sample lines which can occur with Teflon tubing. A bypass loop was installed on the A-1000 as in the prior experiments. Each instrument was gravity drained. PPT serial numbers 9809-0006 and 9901-0018 had flow rates of 108 and 95 mL/min respectively. The 800 had a flow rate of 188 mL/min and the Thornton 502P-SX had a oxidized sample flow rate of 75.1 mL/min and a bypass flow rate of 394.0 mL/min. The recommended oxidized sample flow rate for the 502P-SX is 75 mL/min so the instrument was ready for operation. The A-1000 had a flow rate of 98 mL/min. The inlet pressure from the UPW system was approximately 60 psig and was reduced to 22.5 psig by the pressure regulator. The results are shown in Chart 32.

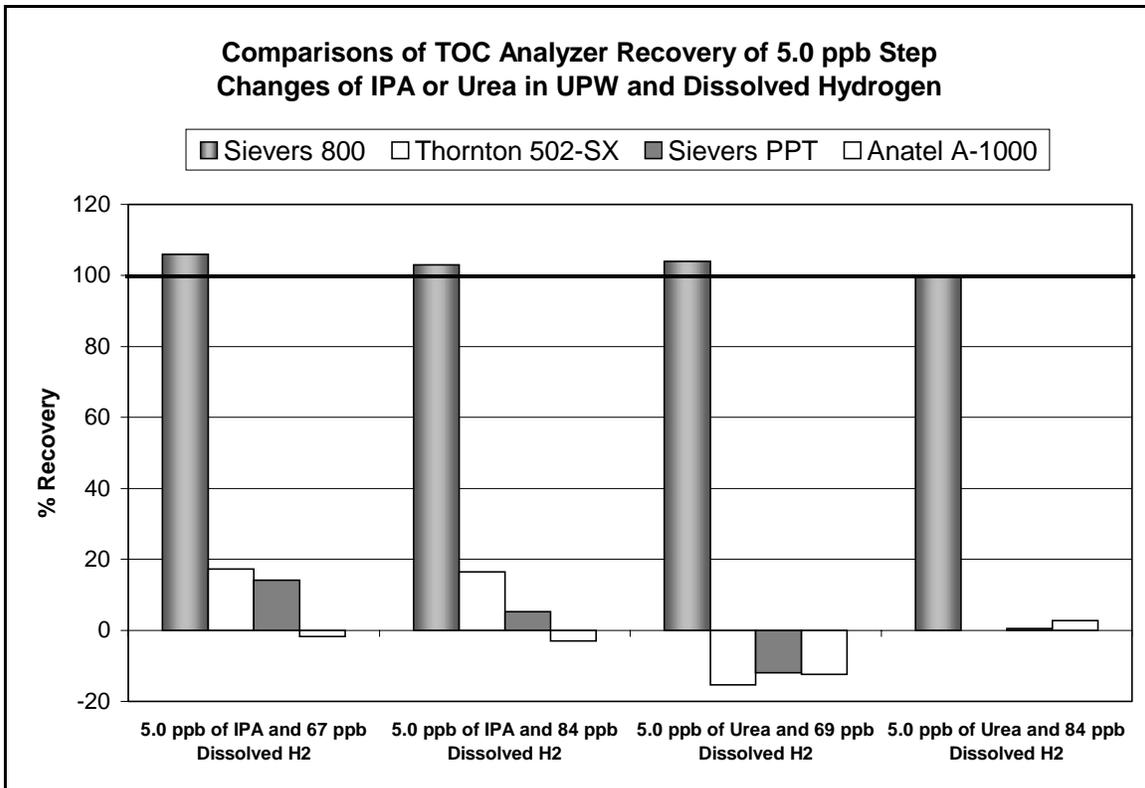


Chart 32: Comparisons of TOC Recovery of 5 ppb IPA or Urea in UPW and Dissolved H₂ at the Arizona Test Site.

It is clear the reagentless TOC analyzers were not able to correctly recover the 5 ppb injections of IPA or Urea. The H₂ clearly lowers the recovery of IPA for the reagentless TOC analyzers and lowers the expected good recovery of the Sievers PPT to urea. The depressed TOC responses experienced at the Japanese and Korean testing sites could be caused by the presence of some type of residual reducing agent in the UPW, such as dissolved H₂. The Sievers 800 with the internal oxidizer addition was able to completely recover both compounds.

Summary

The recovery data for the Colorado, Oregon, Japanese, and Korean study sites is summarized by TOC analyzer in the following charts 33,34, and 35.

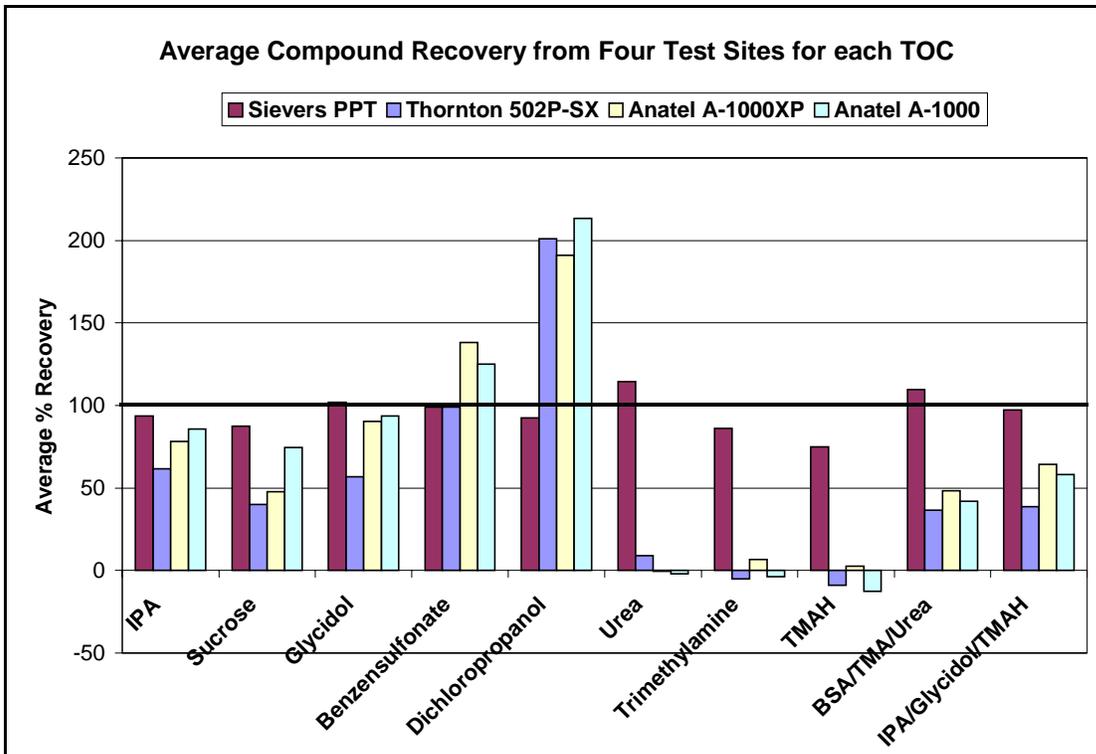


Chart 33: Overall Average Compound Recovery at Four Test Sites

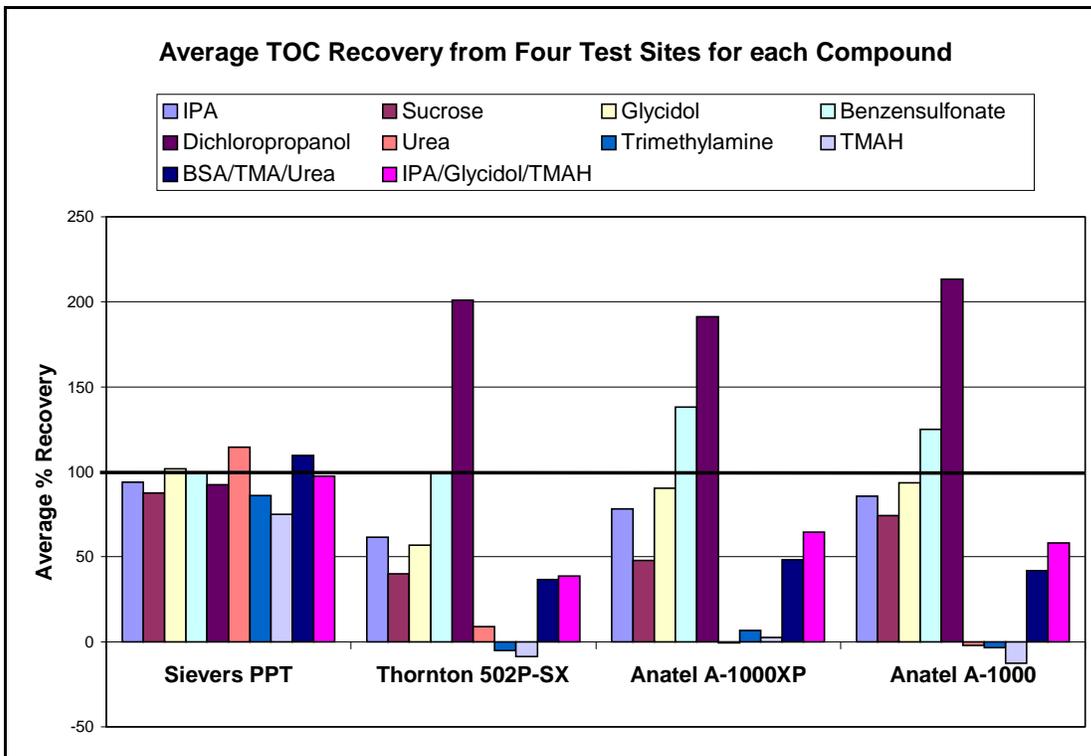


Chart 34: Overall Average Compound Recovery Grouped by TOC Analyzer

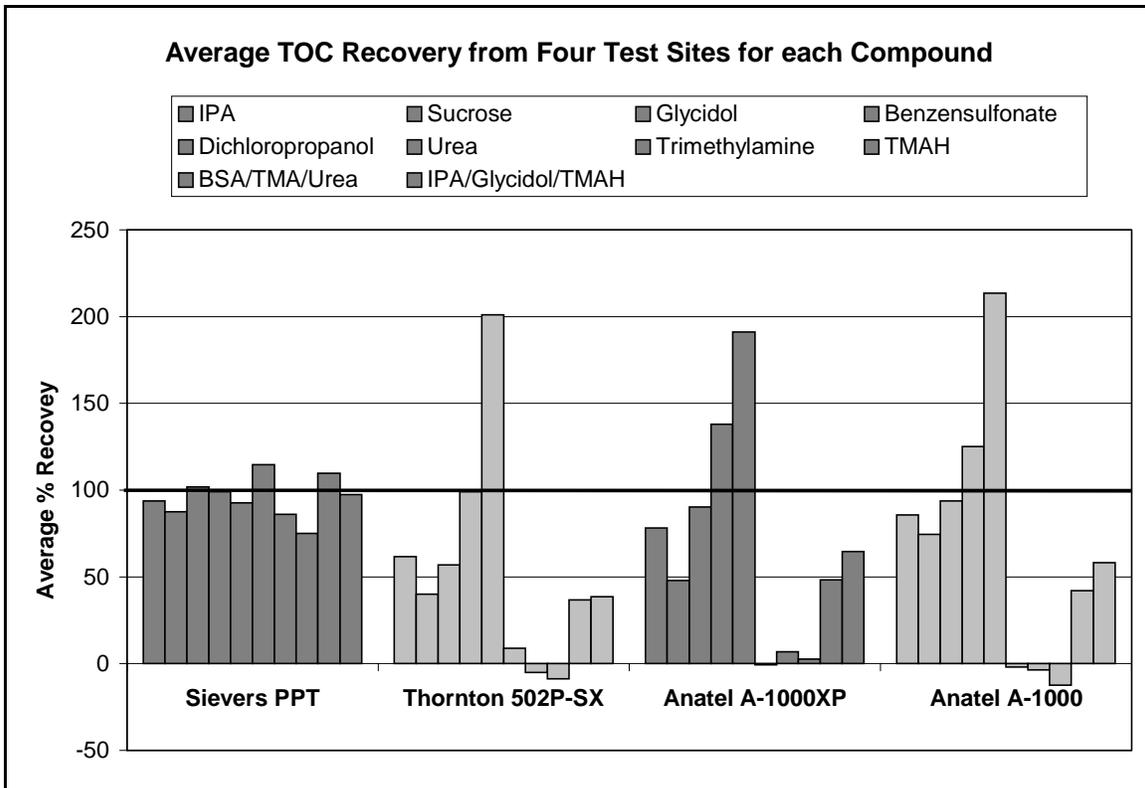


Chart 35: TOC Analyzers Viewed Relative to Overall 100% Recoveries in UPW.

Compound Recovery

The last three charts highlight the recovery problems of three TOC analyzers, Thornton 502P, Anatel A-1000XP, and the Anatel A-1000. The Sievers PPT shows good recovery.

Organic Nitrogen Compounds:

The Thornton and both Anatel TOC's all show a surprising problem with recovery of organic nitrogen compounds. It is speculated that these analyzers are not oxidizing this class of compounds. If these compounds were oxidized completely, one would expect a greater than 100% recovery due to measurement errors from the nitrate ion (10) in these analyzers, but this was not seen. Mizuniwa et al. (8) have shown organic nitrogen compounds are present in relatively high amounts in ultrapure water systems. These two facts increase the probability that these three TOC analyzers will produce incorrect TOC results in ultrapure water systems.

Chlorinated Organic Compounds:

The same three analyzers show very high responses to chlorinated organic compounds. The two test compounds chloroform (Chart 6) and dichloropropanol (Charts 19, 25, 31,

and 33) all show high recoveries for three of the TOC analyzers the Thornton 502P, Anatel A-1000XP, and the Anatel A-1000. This result was not unexpected as it has been shown by Chu (10) that UPW TOC analyzers using direct conductivity detection are subject to the problem of misinterpreting the strong acids formed after oxidation from halogenated organics. This results in higher than 100% recovery.

Sievers PPT:

In contrast to these three TOC analyzers results, the Sievers PPT recovers both classes of compounds very well. Chart 35 shows the Sievers PPT analyzer to have the best overall compound recovery accuracy of the four tested UPW TOC analyzers.

Precision and Stability

Precision:

The results of a statistical analysis of IPA standard injections at the Oregon test site show the 90% confidence limits on TOC measurements for each analyzer (Chart 8). These results are summarized in Table 13.

Table 13: TOC Measurement 90% Confidence Limits on IPA

	PPT	502P-SX	A-1000XP	A-1000
90% Confidence Limits on Measurements (ppb)	± 0.02	± 0.06	± 0.07	± 0.10

The Sievers PPT showed the highest precision of the four analyzers.

Stability:

Instrument to instrument and test site to test site instrument performance showed good reproducibility for the Anatel A-1000XP, Anatel A-1000 and the Sievers PPT.

When the water and air temperature was greater than 32 °C the A-1000XP would switch from XP mode to A-1000 mode. This resulted in poor stability at 32 °C.

The Thornton 502P showed marked changes in recovery under these conditions. It is speculated that the intensity of the UV lamp (age) and the variations in flow rate of the sample could change the recovery for this analyzer.

The standard addition device appeared to contribute approximately ± 0.01 ppb to the standard deviation of compound injection measurements.

Dissolved H₂ in UPW

All reagentless UPW TOC analyzers (A-1000XP, A-1000, 502P, and PPT) showed very poor compound recovery when dissolved H₂ was present in the UPW at levels of 67 ppb and greater. The reagent based Sievers 800 was able to oxidize the compounds well enough to get very close to 100% recovery under these conditions.

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Biography

The author, Richard Godec is the New Product Development Manager at Ionics-Sievers Instruments in the USA. He has over 21 years experience in the design, development and manufacturing of analytical instrumentation supporting both process and laboratory applications in the pharmaceutical, semiconductor, power, petrochemical, and medical industries. He has been responsible for the development of new analyzers for measurement of total organic carbon in water and organic sulfur in petrochemicals. Mr. Godec holds over 18 patents in these fields. Prior to joining Sievers twelve years ago, he

was a co-founder of Anatel Instrument Corporation. Mr. Godec holds a B.Sc. in Chemical Engineering from the University of Colorado.

References

- 1) Godec R, Franklin K. "The Verification of Analytical Ultrapure Water Instrumentation Performance using an Automated Standard Dilution Apparatus". Semiconductor Pure Water and Chemicals Conference, pp. 91-110, 1999.
- 2) Gottlieb M, Meyers P. "The Production of Ultra Low TOC Resins". Semiconductor Pure Water and Chemicals Conference, pp. 23-42, 1998.
- 3) Bollinger MJ, Craig CA, Godec R, Kosenka P, O'Neill K. "A Novel Approach to Verifying TOC Instrument Accuracy". Semiconductor Pure Water and Chemicals Conference, pp. 97-109, 1997.
- 4) Pate KT. "DI Water Resistivity versus Trace Ion Levels". Ultrapure Water, pp. 26-33, Vol. 8, No. 1, Jan./Feb., 1991.
- 5) Cutler CM. "Measurement of Cation Resin Extractables". Ultrapure Water, pp. 40-48, Vol. 5, No. 6, Sept., 1988.
- 6) Emery AP, Girard JE, Jandik P. "Investigation of Pure Water Contaminants Stemming From Ion Exchange Materials". Ultrapure Water, Oct, 1988.
- 7) Personal communications with Kurita R&D personnel, June 1997.
- 8) Mizuniwa T, Kitami K, Ito M, Miwa R. "Analysis of Organic-combined Chloride, Sulfate and Nitrate Ions in Ultrapure Water". Semiconductor Pure Water and Chemicals Conference, pp. 111-124, 1999.
- 9) Govenal RA, Shadman F. "Design of High-Purity Water Plants: Fundamental Interactions in Removal of Organic Contamination". Ultrapure Water, Sep, 1992.
- 10) Chu, Theresa "Trihalomethanes Can Cause RO/DI System Problems". Semiconductor Pure Water Conference, 1989.
- 11) Zhu WH, DeGenova J, Craig C, Godec R. "Effective Monitoring of Organic Contaminants in Water Recycling Systems". Semiconductor Pure Water and Chemicals Conference, pp. 113-120, 1998.
- 12) Skoog DA, West DM (1980) *Analytical Chemistry*, 3rd edition, Philadelphia: Holt, Rinehart and Winston.

- 13) Anderson RL (1987) *Practical Statistics for Analytical Chemists*. New York: Van Nostrand Reinhold.
- 14) Caulcutt R and Boddy R (1983) *Statistics for Analytical Chemists*. London: Chapman and Hall.
- 15) Kleinbaum DG, Kupper LL and Miller KE (1988) *Applied Regression Analysis and Other Multivariable Methods*, 2nd edition, Boston: PWS-Kent.
- 16) Meier PC and Zund RE (1993) *Statistical Methods in Analytical Chemistry*. New York: Wiley Interscience.
- 17) Miller JC and Miller JN (1993) *Statistics for Analytical Chemistry*, 3rd edition, Chichester: Ellis Horwood PTR Prentice Hall.