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TOC Solutions

Harnessing the power of Total Organic Carbon Analyzers

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Fast Facts

♦ Find it on the web

The study that this application note is based on can be found on our web site. Just go to the TOC PPT section of www.sieversinst.com to read the full study.

♦ For more information

We welcome your feedback and questions. Please contact Will McHale, TOC product specialist at wmchale@sieversinst.com or at 303.444.2009.

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IONICS

Instrument Business Group

Comparison of TOC Recovery in Ultrapure Water

Objective

To characterize the variation in TOC concentrations observed by our customers using different TOC measuring technologies on the same water supply.

Conclusion

Older on-line TOC methods are prone to significant analytical error when measuring organic compounds typically present in ultrapure water. These non-selective methods tend to over or under recover TOC depending upon the type of organic contamination present.

Discussion

The complete recovery of organic compounds contained in working samples is critical to the analytical accuracy of TOC instrumentation. The following study was undertaken to investigate the recovery efficiencies of various types of TOC instrumentation.

At four customer sites, a series of standard additions were conducted to compare the recovery efficiencies of several different TOC technologies. TOC instruments tested included Anatel's A-1000 & A-1000XP, Thornton's 502P, and the Sievers' Ultrapure PPT. Organics of interest to the semiconductor industry were added through a standard dilution device[1] at levels ranging from 0.1 ppb to 2.5 ppb TOC. These organics were chosen based on the likely probability of their occurrence in the final product water produced by modern ultrapure water (UPW) systems.

It is well established that organic nitrogen compounds are an important fraction of the TOC found in UPW[3]. Empirical data (Figure 1)[2] shows that the A-1000, A-1000XP and 502P were unable to recover organic nitrogen compounds. By contrast, the Ultrapure PPT instrument showed complete recovery of these compounds. The details of this study can be found in a paper by R. Godec presented at the 2000 Semiconductor Pure Water and Chemicals Conference (SPWCC)[2].

The reason(s) for the poor recoveries exhibited by the A-1000, A-100, A-1000XP, and 502P is not known. It could be attributed to their low oxidative efficiencies or mass transport problems in the oxidation reactors. It may also be attributed to the unusual oxidation chemistries of low concentrations of organic nitrogen compounds and a combination of factors including the method of CO_2 detection.

CO_2 Measurement Methods

The Anatel and the Thornton TOC analyzers use a direct conductometric measurement of the oxidation products to determine TOC, while the Sievers PPT uses a CO_2 selective membrane-conductometric method.

The data also reveals that in the case of dichloropropanol, only the Sievers PPT was accurate. The A-1000, A-1000XP and 502P all reported exaggerated levels; two or more times actual in each case. The Anatel's positive interference with halogenated compounds was reported in 1989 by Balazs Analytical Laboratory[4]. With the exception of the Sievers PPT (which uses a patented CO_2 selective membrane conductometric

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measurement), the other instruments measure sample conductivity directly after oxidation. In this case they measure the byproducts of the dissociation of the dichloropropanol (H^+, Cl^-) in addition to the desired HCO_3^-.

Comparison of Oxidation Cells

Sievers' and Anatel's oxidation cell geometries are shown in Figures II and III. Figure II shows the A-1000 cell is circular, with a quartz top and two titanium electrodes. The water sample occupies an interior depth of 0.36 inches around the circular electrode. The UV lamp is positioned on top of the quartz. Figure III shows the Sievers PPT uses an efficient synthetic fused silica reaction tubular coil reactor. The inside diameter on the coil is slightly greater than one millimeter.

UV_{185} is critical for formation of hydroxyl radicals (HO·), the key oxidants in UV-promoted oxidation. Based on the penetration of UV_{185} through water, we estimate that only 33% of the UV_{185} irradiation reaches the bottom of the cell, in the Anatel A-1000, at a depth of 0.36 inches. In contrast, the Sievers PPT reactor design allows at least 85% of the UV to reach all areas of the oxidation reactor. The reduced penetration of UV_{185} may account for Anatel's lower organic recovery problems.

Summary

Data from standard addition experiments has revealed the inability of the A-1000, A-1000XP and 502P to recover Urea, TMA, TMAH and dichloropropanol accurately. These analyzers underreported some compounds and exaggerated others.

A comparison of Anatel's and Sievers' technologies reveals differences in the oxidation cell geometry and CO_2 measurement methods. This is one possible explanation for recovery differences.

Based on the results from the realistic testing program, the Sievers PPT TOC Analyzer did not suffer from positive or negative organic recovery problems and can be assumed to provide complete and accurate TOC measurements in ultrapure water.

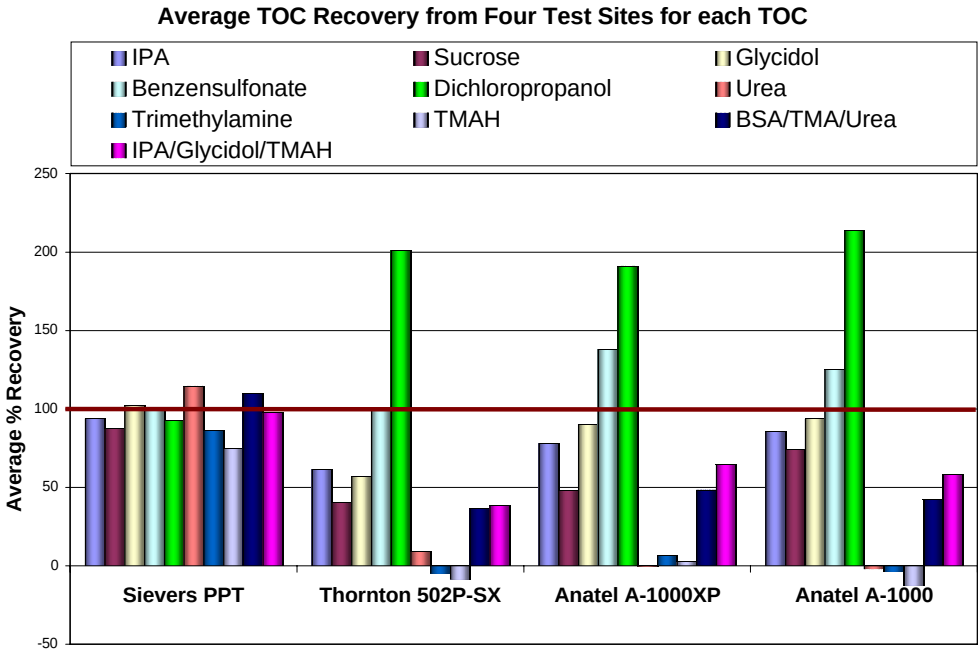

Figure I. *Average TOC Recovery for several compounds at four test sites*

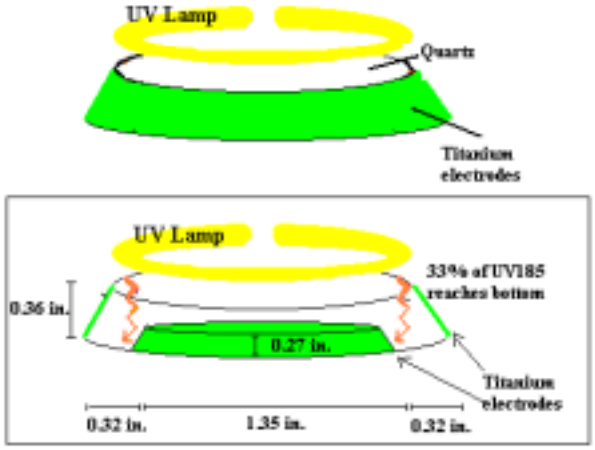

Figure II. *Anatel's Oxidation Cell*

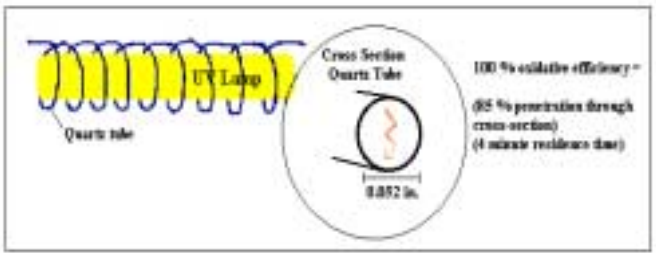

Figure III. *Sievers Continuous Flow Oxidation Cell*

References

[1] Godec, Rick; Franklin, Karen; "The Verification of Analytical Ultrapure Water Instrumentation Performance using an Automated Standard Addition Apparatus", Semiconductor Pure Water and Chemical Conference, pp. 91-110,1999.

[2] Godec, R; "The Performance Comparison of Ultrapure Water TOC Analyzers using an Automated Standard Addition Apparatus", SPWCC, pp. 61-112, 2000.

[3] Mizuniwa T. et al; "Analysis of Organic-combined Chloride, Sulfate and Nitrate Ions in Ultrapure Water"; SPWCC, pp. 111-124, 1999.

[4] Chu, T.; "Trihalomethanes Can Cause RO/DI System Problems"; Semiconductor Pure Water Conference, 1989.[1] Godec, Rick; Franklin, Karen; "The Verification of Analytical Ultrapure Water Instrumentation Performance using an Automated Standard Addition Apparatus", Semiconductor Pure Water and Chemical Conference, pp. 91-110,1999.