New Breakthrough in Wet Chemical TOC Analysis

Humic Acid: A Complex Molecule, A Simple Solution

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Abstract

The goal of this discussion is to demonstrate that the Shimadzu TOC-V_W can effectively oxidize the Humic Acid (HA) matrix at high accuracy and precision levels never before witnessed by the wet chemical TOC community. The Shimadzu TOC-V_W Carbon analyzer is the only TOC on the market that uses three oxidation techniques of UV light, Heat, and persulfate in a single analyzer. Due to this advancement in Wet Chemical TOC technology, difficult to oxidize compounds such as HA can now be efficiently analyzed with high levels of accuracy and precision. This makes life significantly easier for members of the drinking water community who prefer a wet chemical TOC analyzer to a combustion TOC analyzer.

Introduction

What is Humic Acid (HA) and what is its importance? If you are not a soil scientist, these are the types of questions that you may have. HA is a highly complex polymeric substance found in virtually every scoop of soil. It can be characterized at best as a mixture of polymers containing aromatic and heterocyclic structures, carboxyl groups and nitrogen. It is important in soil chemistry due to its excellent chelating properties as well as its buffering capacity. In environmental water chemistry, HA is also of importance, since it is a natural stream pollutant. Also, it is thought to be capable of triggering the “red tide” phenomenon due to microorganisms in seawater.[1] It is of extreme current interest due to the fact that it is a disinfectant byproduct (DBP) precursor. DBP’s are toxic and potentially carcinogenic. DBP’s are reported to cause bladder and colon cancer in ~10,000 people annually in the United States. During the drinking water treatment process, HA will form the DBP’s of chloroform and other haloforms once the water has been treated with chlorine. To add, if the water source contains other halogens such as bromide and iodide ions, bromoforms and iodoforms will be formed in the same way.[2]

With respect to TOC analysis, HA is considered to be the most difficult compound to measure due to its solubility characteristics and highly polymeric matrix. At pH <2, HA is completely insoluble in water. Thus, when performing the acidify and sparge method of TOC, otherwise known as Non-Purgeable Organic Carbon (NPOC), it can easily precipitate out of solution and cause significantly low recoveries. Also, because of the bulkiness of the HA molecule, it is extremely difficult to oxidize.

The Environmental Protection Agency requires that a great deal of municipal water managers monitor the DBP levels by measuring the TOC of the influent and treated waters. Obviously, since HA comprises a large portion of natural stream and river waters, TOC results can be adversely affected at municipal drinking water treatment facilities. Difficulty in efficiently oxidizing the HA molecule during TOC analysis has been a grappling issue for the TOC community for the past 15 years.

Standard Methods 5310 has established that for difficult matrices such as HA, the most suitable TOC method is high temperature combustion. High temperature combustion TOC can efficiently recover HA matrices in the range of 100%. In the past, wet chemical TOC’s have failed miserably at measuring relatively high levels of HA. Other TOC manufacturers have reported HA recoveries at only 80% using conventional wet chemical methods.

Method

A Shimadzu TOC-V_C (Combustion) and TOC-V_W (Wet Chemical) were configured for side by side analysis of HA solutions prepared at 1ppm, 10ppm, and 50ppm concentration levels. The NPOC method was incorporated for both instruments. NPOC calibration curves were prepared for both instruments using Potassium Hydrogen Phthalate (KHP). The first calibration curve was constructed using 0, 1, and 10 ppm KHP standards. The second calibration curve was constructed using 0, 10, and 50 ppm KHP standards. All samples were automatically pH adjusted by the instrument to achieve optimum NPOC results. Samples were sparged for three minutes following acid addition to optimize Inorganic Carbon (IC) removal. All HA solutions were analyzed and compared using both the TOC-V_C and TOC-V_W systems.

Results

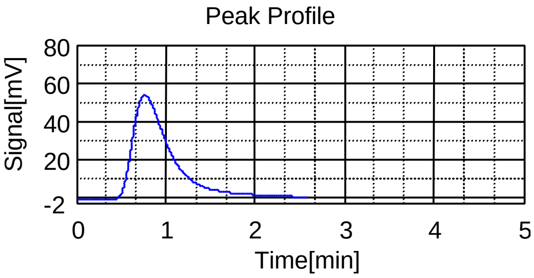
Section 1: TOC-V Wet Chemical versus Combustion for 1ppm Humic Acid Solution

A 1 ppm HA solution was analyzed using the TOC-V Wet Chemical and Combustion analyzers. For each oxidation method, results were compared against a 1 ppm KHP control standard using a 0, 1, and 10 ppm KHP calibration curve. In Table 1, the 1ppm KHP control yielded actual concentrations of 0.9977 and 1.001 ppm for the wet chemical and combustion method, respectively. The 1 ppm HA gave actual concentrations of 1.017 and 1.011 ppm for the wet chemical and combustion, respectively. Also, Graphs 1 and 2 show the peak profiles for the 1ppm HA using wet chemical and combustion, respectively. The analysis time is just under 3 minutes for the wet chemical and just over 2 minutes for the combustion.

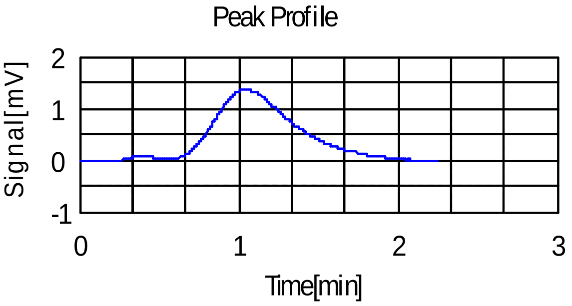
Table 1: 1 ppm Humic Acid Analysis

Sample	Wet Chemical (TOC-V_W)			Combustion (TOC-V_C)		
	Actual	% Recovery	CV	Actual	% Recovery	CV
1 ppm Control (KHP)	0.9977	99.77	0.460	1.001	100.1	0.7600
1 ppm Humic Acid	1.017	101.7	3.69	1.011	101.10	3.08

Graph 1: 1 ppm Humic Acid TOC-V_W



Graph 2: 1ppm Humic Acid TOC-V_C



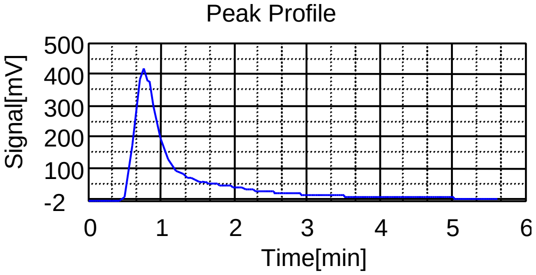
Section 2: TOC-V Wet Chemical versus Combustion for 10ppm Humic Acid Solution

A 10 ppm HA solution was analyzed using the TOC-V Wet Chemical and Combustion analyzers. For each oxidation method, results were compared against a 10 ppm KHP control standard using the 0, 1, and 10 ppm KHP calibration curve. In Table 2, the 10 ppm KHP control yielded actual concentrations of 10.07 and 10.31 ppm for the wet chemical and combustion method, respectively. The 10 ppm HA gave actual concentrations of 9.731 and 10.07 ppm for the wet chemical and combustion, respectively. Also, Graphs 3 and 4 show the peak profiles for the 10 ppm HA using the wet chemical and combustion, respectively. The analysis time is just under 6 minutes for the wet chemical and approximately 3 minutes for the combustion.

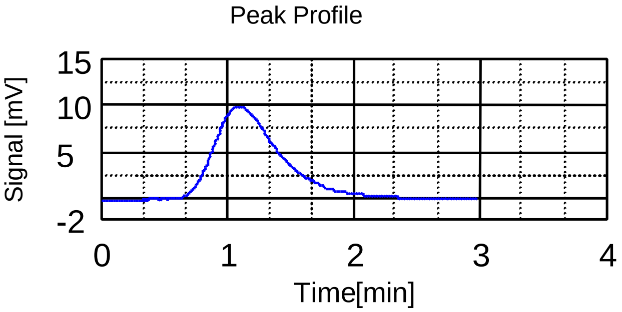
Table 2: 10 ppm Humic Acid Analysis

Sample	Wet Chemical (TOC-V_{WS})			Combustion (TOC-V_{CSH})		
	Actual	% Recovery	CV	Actual	% Recovery	CV
10 ppm Control (KHP)	10.07	100.7	1.34	10.31	103.1	1.76
10 ppm Humic Acid	9.731	97.31	1.64	10.07	100.7	1.79

Graph 3: 10 ppm Humic Acid TOC-V_W



Graph 4: 10 ppm Humic Acid TOC-V_C



Section 3: TOC-V Wet Chemical versus Combustion for 50ppm Humic Acid Solution

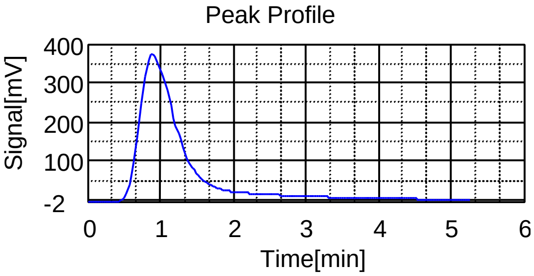
A 50 ppm HA solution was analyzed using the TOC-V Wet Chemical and Combustion analyzers. For each oxidation method, results were compared against a 50 ppm KHP control standard using the 0, 10, and 50 ppm KHP calibration curve. In Table 3, the 50 ppm KHP control yielded actual concentrations of 49.52 and 50.04 ppm for the wet chemical and combustion method, respectively. The 50 ppm HA gave actual concentrations of 45.58 and 50.53 ppm for the wet chemical and combustion, respectively. Also, Graphs 5 and 6 show the peak profiles for the 50 ppm HA using the wet chemical and combustion, respectively. The analysis time is just under 6 minutes for the wet chemical and approximately 4 minutes for the combustion.

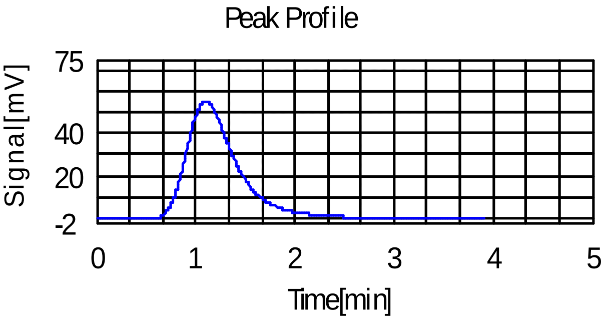
Table 3: 50 ppm Humic Acid Analysis

Sample	Wet Chemical (TOC-V_{WS})			Combustion (TOC-V_{CSH})		
	Actual	% Recovery	CV	Actual	% Recovery	CV
50 ppm Control (KHP)	49.52	99.04	0.69	50.04	100.1	1.26
50 ppm Humic Acid	45.58	91.16	0.95	50.53	101.1	1.37

Graph 5: 50 ppm Humic Acid TOC-V_W

Graph 6: 50 ppm Humic Acid TOC-V_C





Conclusion

It is important to reiterate that in years past, HA is a difficult compound to oxidize at 1ppm and 10ppm levels. Achieving recoveries in the range of 90% for 10 ppm HA is typical of other commercially available wet chemical TOC analyzers. Thus, achieving percent recoveries close to 100% at 1 ppm and 10 ppm is truly an accomplishment for the TOC-V_W. At higher levels of 50ppm and greater, it becomes even more evident that this substance poses a dilemma in TOC analysis. Other commercially available wet chemical methods show recoveries around 80% at the 50 ppm range. Thus, achieving percent recoveries above 90% at the 50 ppm range is also a major achievement for the TOC-V_W. Consider that most natural streams contain on the order of 5 ppm TOC, and HA comprises 50 to 70% of the TOC present in these waters. The TOC-V_W is able to efficiently analyze on the order of ten to twenty times higher the amounts of HA typically found naturally in the environment. Furthermore, compared to other TOC manufacturers, this results in approximately a 10% increase in the recovery of HA across three orders of magnitude using the TOC-V_W analyzer.

From analyzing the results of the HA solutions prepared in this study, it is shown that the TOC-V_W analyzer efficiently oxidizes this complex molecule with high precision and accuracy. From Tables 1, 2, and 3, the percent recoveries of 1, 10, and 50 ppm HA solutions are 101.7%, 97.3%, and 91.2%, respectively. The coefficient of variations for the 1, 10, and 50ppm HA solutions are 3.69%, 1.64%, and 0.95%, respectively. The percent recoveries of the 1, 10, and 50 ppm KHP control solutions are 99.8%, 100.7%, and 99.0%, respectively. When comparing the peak profiles of the HA solutions at all concentration ranges, the combustion method has expected faster analysis times with respect to the wet chemical method. The average analysis times for the wet chemical and combustion methods are approximately 4.5 minutes and 3 minutes, respectively. However, the efficiency of the TOC-V_W is witnessed in the fact that the HA molecule has extremely high recovery rates compared to previous TOC wet chemical instruments on the market. Also, all of the HA solutions exhibit no tailing in their peak profile behavior. Meaning, the molecule is completely oxidized. Although analysis time is an important issue with respect to analytical instrumentation, it is equally important to ensure that all substances, from easy-to-oxidize to difficult-to-oxidize are being analyzed with high accuracy and precision. This holds especially true for HA, a complex molecule that not only happens to occur naturally in our environment, but also functions as a tremendous disinfectant byproduct precursor. Also, the inherit difference between the responses of the wet chemical and combustion instruments is seen in the peak profiles. Since, the wet chemical instrument utilizes larger injection volumes than the combustion instrument, the response is also significantly larger. The fact that the wet chemical instrument can efficiently oxidize a large amount of a difficult-to-oxidize substance, such as HA, demonstrates the power of having three forms of oxidation, UV, heat and persulfate, all housed into a single analyzer.

References

1. Hawley's Condensed Chemical Dictionary 11th Edition, Humic Acid, 609.
2. Steelink, C. Analytical Chemistry, 2002, Investigating Humic Acids in Soils, 327A, 332A.