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A comparison of three TOC methods on a single analyzer

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In the past, persulfate-based total organic carbon (TOC) analyzers were noted for their ability to achieve highly sensitive TOC analysis. However, with the advantages came disadvantages. Persulfate-based oxidation works very efficiently for clean water matrices. However, the oxidation begins to decrease in efficiency as matrices become more complex. Standard Methods 5310 notes that, with respect to combustion oxidation, persulfate-based oxidation cannot efficiently oxidize substances that contain high-molecular-weight compounds, high salts, and high particulates. The persulfate-based TOC analyzers that are commercially available have attempted to address the efficiency drawbacks by offering the UV light and persulfate (UP) oxidation method, due to the fact that ultraviolet light is an excellent oxidizer of carbon-based materials. Other manufacturers offer the heat and persulfate (HP) oxidation method, due to the fact that the reaction rate increases when the temperature of the reaction is increased.

Realizing that the wet chemical TOC of the future must address the need for further optimizing the efficiency of the wet chemical TOC oxidation process, **Shimadzu Scientific Instruments** (Columbia, MD) developed the TOC-V_W Wet Chemical Series TOC analyzer, which incorporates the UV light, heat, and persulfate (UHP) oxidation method in a single instrument. The advantages of the UHP wet chemical oxidation technique are numerous. By combining UV light, heat at 80 °C, and persulfate the analyst will achieve better accuracy and faster analysis times, and decrease persulfate consumption.

Another advantage comes from the standpoint of maintenance. The analyzer can handle particulate sizes up to 800 µm. Thus, the potential for clogs is greatly reduced for sample matrices that contain particulates. Other analyzers experience clogs in the instrument flow path if particle sizes are above 100 µm. Furthermore, by incorporating a UHP method, the concern of the intensity of the UV lamp dissipating over time becomes minor. As the UV lamp ages, the combination of heat and persulfate will ensure that the oxidation is carried to completion. This way, the user does not experience an interruption in analysis while waiting for a replacement UV lamp.

Method

Using the UHP method, three total carbon (TC) calibration curves are created at three different ranges covering three orders of magnitude. Samples are analyzed at 0.5-, 5.0-, and 50-ppm concentration levels for various organic compounds using the UHP, UP, and HP oxidation methods. The first oxidation method is the UHP method, the second is the UP method, and the third is the HP method. All of the oxidation methods are analyzed using the three different oxidation methods, and 1.5 mL of persulfate reagent is automatically added to each sample.

In the first sample study, typical United States Pharmacopeia (USP) standards of 0.5-ppm sucrose and 0.5-ppm 1,4-benzoquinone (1,4-BQ) are analyzed against the low-level calibration curve.

In the second sample study, 5-ppm TC standards are prepared of the following organic compounds: potassium hydrogen phthalate (KHP), benzoic acid, oxalic acid, and glycine. These compounds are analyzed against the midlevel curve, 0–5 ppm.

The third sample study includes the analysis of several 50-ppm TC standards including KHP, benzoic acid, glycine, nicotinic acid, and ethylenediaminetetraacetic acid (EDTA) using the high-level calibration curve, 0–50 ppm.

In the final study, a cross-examination of the various organic compounds at different concentration ranges is conducted. The UP and HP methods are employed using double the persulfate volume, 3.0 mL, that is used in the previous studies. The UHP method is conducted using the normal 1.5-mL persulfate volume.

Results

The UHP method gives the best recoveries with an actual concentration of 0.484 ppm for the 0.5-ppm sucrose standard and an actual concentration of 0.514 ppm for the 0.5-ppm 1,4-BQ standard (see *Table 1*). The UP method gives lower but similar results for both the 0.5-ppm sucrose standard and the 0.5-ppm 1,4-BQ standard. However, the HP method gives significantly lower results for both the 0.5-ppm sucrose standard and the 1,4-BQ standard. In addition, the UHP method gives the fastest analysis time

Table 1

Oxidation efficiency comparison using 0.5-ppm USP standards

Compound		**UV, heat, persulfate**			**UV, persulfate**			**Heat, persulfate**	
	Conc.	SD	CV	Conc.	SD	CV	Conc.	SD	CV
Sucrose	**0.484**	0.0044	0.92	**0.478**	0.0040	0.96	**0.365**	0.0012	0.31
1,4 BQ	**0.514**	0.0059	1.16	**0.471**	0.0177	4.20	**0.341**	0.0032	0.44
					Analysis time (min)				
Compound		**UV, heat, persulfate**			**UV, persulfate**			**Heat, persulfate**	
Sucrose		2.05			2.44			3.51	
1,4 BQ		2.09			2.77			3.76	

Table 2

Oxidation efficiency comparison using various organic carbon compounds prepared at 5-ppm

Compound		**UV, heat, persulfate**			**UV, persulfate**			**Heat, persulfate**	
	Conc.	SD	CV	Conc.	SD	CV	Conc.	SD	CV
KHP	**5.054**	**0.0095**	**0.19**	**4.981**	0.0136	0.27	**4.831**	0.1433	2.86
Benzoic acid	**5.121**	0.0315	0.62	**5.005**	0.0068	0.14	**4.719**	0.1518	3.22
Oxalic acid	**5.181**	0.0273	0.53	**5.264**	0.0113	0.22	**5.181**	0.0296	0.57
Glycine	**5.269**	0.0235	0.45	**5.008**	0.0143	0.29	**4.947**	0.0972	1.96
					Analysis time (min)				
Compound		**UV, heat, persulfate**			**UV, persulfate**			**Heat, persulfate**	
KHP		2.46			3.54			4.13	
Benzoic acid		2.46			3.64			4.24	
Oxalic acid		2.11			2.55			2.26	
Glycine		2.44			3.57			5.51	
Average analysis time		**2.37**			**3.33**			**4.04**	

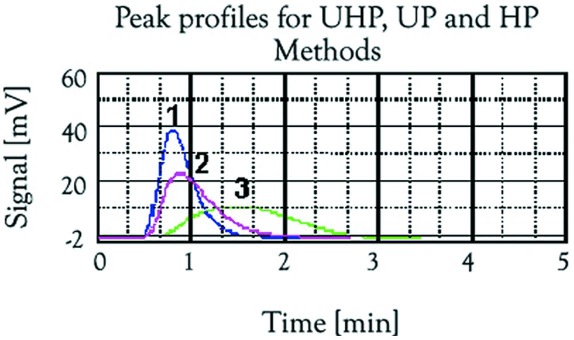

Figure 1 *Analysis times of 0.5-ppm 1,4-BQ using UHP, UP, and HP methods.*

of 2.05 min for the sucrose standard and 2.09 min for the 1,4-BQ standard. The analysis times of these same standards are significantly longer using the UP and HP methods. The UHP method shows similar analysis times for the easily oxidized sucrose and the hard-to-oxidize 1,4-BQ at 2.05 and 2.09 min, respectively. The UP and HP methods clearly show increases in the analysis time of the difficult-to-oxidize 1,4-BQ. The persulfate concentration is 10.5%. The flow rate of the TOC-V$_W$ is 200 mL/min, and the flow pathlength is held constant. These instrument conditions are the same for all three oxidation methods.

Figure 1 shows the signal (mV) vs time (min) plot for the analysis times of 0.5-ppm 1,4-BQ using the UHP, UP, and HP methods. Peak 1 represents the UHP method with an analysis time of 2.09 min. Peak 2 represents the UP method with an analysis time of 2.77 min. Peak 3 represents the HP method with an analysis time of 3.76 min. Peak 1 shows that the UHP method produces a much sharper peak and, by removing the heat, the peak broadens, as seen with peak 2 of the UP method. When the HP method is used, the resultant peak 3 is the broadest of all the methods. The peak profile characteristics of the 0.5-ppm sucrose standard using the UHP, UP, and HP methods are similar to the 1,4-BQ standard. Table 1 and Figure 1 clearly demonstrate that the UHP method is the most efficient for the oxidation of compounds in the 0–0.5 ppm concentration range.

The recoveries and analysis times of several 5-ppm organic compounds are compared with respect to the different oxidation methods (see *Table 2*). The recoveries for all three oxidation methods are similar. However, the analysis times are significantly faster for the UHP method. Considering that different compounds will naturally have different analysis times, an average analysis time trend with respect to a particular oxidation method is observed. The average analysis times are 2.37, 3.33, and 4.04 min for the UHP, UP, and HP methods, respectively. The persulfate concentration is 10.5%. The flow rate of the TOC-V$_W$ is 200 mL/min, with the flow pathlength held constant. These instrument conditions are the same for all three oxidation methods.

Figure 2 shows the signal (mV) vs time (min) for the analysis of a 5-ppm KHP standard using the UHP, UP, and HP methods. Peak 1 represents the UHP method with an analysis time of 2.46 min. Peak 2 represents the UP method with an analysis time of 3.54 min. Peak 3 represents the HP method with an analysis time of 4.13 min. Peak 1 has the sharpest peak shape. Peak 2 shows more broadening. Peak 3 is the broadest

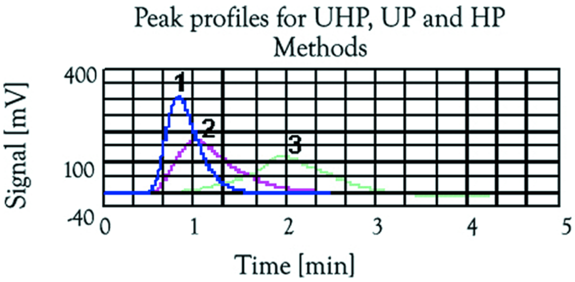

Figure 2 *Analysis times of 5-ppm KHP using UHP, UP, and HP methods.*

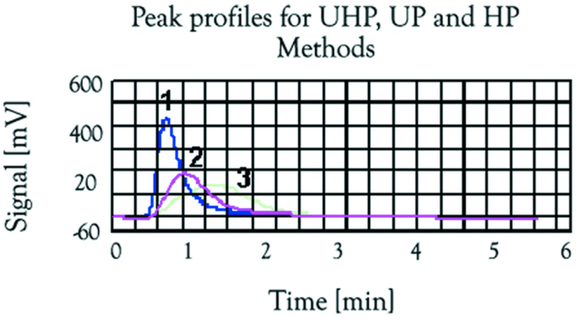

Figure 3 *Analysis times of 50-ppm nicotinic acid using UHP, UP, and HP methods.*

Table 3

Oxidation efficiency comparison using various organic compounds prepared at 50 ppm

Compound	**UV, heat, persulfate**			**UV, persulfate**			**Heat, persulfate**		
	Conc.	SD	CV	Conc.	SD	CV	Conc.	SD	CV
KHP	**49.65**	0.1026	0.21	**48.71**	0.5034	1.03	**38.45**	0.9805	2.07
Benzoic acid	**48.79**	0.4166	0.85	**46.29**	1.063	2.30	**34.38**	1.721	2.36
Glycine	**49.82**	0.0941	0.19	**44.07**	0.8985	2.04	**46.82**	3.672	4.68
Nicotinic acid	**49.88**	0.7076	1.42	**46.45**	0.8944	1.93	**41.60**	0.5851	1.26
Urea	**49.99**	0.1648	0.33	**46.86**	0.3338	0.71	**39.28**	0.1411	0.24

Analysis time (min)

Compound	**UV, heat, persulfate**	**UV, persulfate**	**Heat, persulfate**
KHP	2.37	3.89	4.53
Benzoic acid	2.47	4.53	4.68
Glycine	2.61	4.37	5.76
Nicotinic acid	3.87	5.97	6.081
Urea	2.91	3.50	6.365
Average analysis time	**2.84**	**4.45**	**5.48**

peak. The peak profiles trends and analysis time trends hold true for the 5-ppm benzoic acid, oxalic acid, and glycine standards. Table 2 and Figure 2 clearly demonstrate that the UHP method is the most efficient method for the oxidation of compounds in the 0–5.0 ppm concentration range.

Several 50-ppm organic compounds are analyzed using the different oxidation methods (see *Table 3*). The UHP method gives the best recoveries and fastest analysis times for all of the 50-ppm organic compounds. Using the UHP method, 50-ppm nicotinic acid gives an actual concentration and analysis time of 49.88 ppm and 3.87 min, respectively. The UP and HP methods give lower actual concentrations of 46.45 ppm and 41.60 ppm, respectively. Even further, the analysis times of the UP and HP methods are significantly longer at 5.97 min and 6.08 min, respectively. Considering that different compounds will naturally have different analysis times, an average analysis time trend with respect to a particular oxidation method is observed. The average analysis times are 2.84, 4.45, and 5.48 for the UHP, UP, and HP methods, respectively. The persulfate concentration is 10.5%. The flow rate of the TOC-V$_W$ is 200 mL/min, with a flow pathlength that is held constant. These instrument conditions are the same for all three oxidation methods.

Figure 3 shows the signal (mV) vs time (min) plot for the analysis of 50-ppm nicotinic acid using the UHP, UP, and HP methods. Peak 1 represents the UHP method with an analysis time of 3.87 min. Peak 2 represents the UP method with an analysis time of 5.97 min. Peak 3 represents the HP method with an analysis time of 6.08 min. Also, going from peak 1 to peak 3, the peak shapes broaden significantly. The peak profile trends and analysis time trends are similar for the 50-ppm KHP, benzoic acid, glycine, and urea standards. Table 3 and Figure 3 clearly demonstrate that the UHP method is the most efficient method for the oxidation of compounds in the 0–50 ppm concentration range.

The average analysis times of the various organic compounds using the UHP, UP, and HP methods over three different concentration ranges are examined in *Table 4*. The general trend shows that, when the concentration increases in order of magnitude, the analysis time increases for all of the oxidation methods. However, for the UHP method, the increase in analysis time is less than 0.5 min. For the UP and HP methods, the increase in analysis time ranges from 0.4 to 1.44 min. For example, increasing the concentration range from 5.0 ppm to 50 ppm shows an increase in analysis time of 0.47, 1.12, and 1.44 min for the UHP, UP, and HP methods, respectively.

A comparison study is performed in which the persulfate volumes of the UP and HP methods are doubled

Table 4

Average analysis times of the various organic compounds for the concentration ranges of 0.5, 5.0, and 50 ppm using the UHP, UP, and HP oxidation methods

Concentration (ppm)	UV, heat, persulfate	UV, persulfate	Heat, persulfate
0.5	2.07	2.61	3.64
5.0	2.37	3.33	4.04
50	2.84	4.45	5.48

Table 5

Oxidation efficiency comparison of various organic compounds with increased persulfate volumes

Compound	UV, heat, persulfate		UV, persulfate		Heat, persulfate	
Persulfate volume	(1.5 mL)		(3.0 mL)		(3.0 mL)	
	Actual conc.	Analysis time	Actual conc.	Analysis time	Actual conc.	Analysis time
Sucrose	0.4836	2.05	0.487	2.43	0.4213	3.36
1,4-BQ	0.5141	2.09	0.491	2.55	0.4216	3.60
KHP	5.050	2.46	4.979	3.60	5.003	3.94
Benzoic acid	5.121	2.46	5.098	3.58	4.940	3.15
Glycine	49.82	2.61	53.07	4.03	52.02	5.07
Nicotinic acid	49.88	3.87	48.97	5.65	45.36	5.46
Urea	49.99	2.91	49.04	3.32	46.98	4.39
Average analysis time		**2.64**		**3.59**		**4.14**

to 3 mL in order to improve upon the oxidation efficiency demonstrated in Tables 1–3 and Figures 1–3 (see *Table 5*). Meanwhile, the UHP method consumes the normal 1.5 mL of persulfate. Then, several organic compounds of varying concentrations, covering three orders of magnitude, are analyzed using these conditions. As a result of increasing the persulfate volume, the UP and HP methods give improved recoveries and faster analysis times of the various organic compounds. However, the UHP method overall shows the best recoveries for all of the organic compounds. Furthermore, even by doubling the persulfate volumes, as seen with the UP and HP methods, the analysis times are still significantly longer than the analysis times of the UHP method, using half of the persulfate volume. Considering that different compounds will naturally have different analysis times, an average analysis time trend with respect to a particular oxidation method is observed. The average analysis times are 2.64, 3.59, and 4.14 min for the UHP, UP, and HP methods, respectively. The persulfate concentration is 10.5%. The flow rate of the TOC-V_W is 200 mL/min, with the flow pathlength held constant. These instrument conditions are the same for all three oxidation methods.

Conclusion

From analyzing the results of each table, there is trending that results in analyzing various compounds with TOC concentrations of 0.5, 5, and 50 ppm. The first trend shows that there is a marked increase in analysis times when UV light is removed from the oxidation process. This holds true when heat is removed from the wet chemical process. When comparing the efficiencies of the UP and HP methods, it is observed that the UP method gives better recoveries and faster analysis times. Thus, the oxidation power of UV light must be greater than the oxidizing power of heat.

The second trend shows that by increasing the concentration of the various organic compounds, an increase in the analysis times is observed. However, the increase in analysis time is significantly less for the UHP oxidation method, with respect to the UP and HP methods.

A third trend demonstrates that, even with minimal persulfate consumption, the UHP method gives the best recoveries and fastest analysis times. The UP and HP methods show improved oxidation efficiency in terms of recoveries and analysis times with increased persulfate volumes. However, the UHP method will more efficiently oxidize an organic compound with half of the amount of persulfate that is consumed using the UP and HP methods. Also, it should be noted that in trace level wet chemical analysis, the use of more persulfate increases the potential for contamination. Thus, those who use TOC analyzers that require higher amounts of persulfate with respect to the TOC-V_W analyzer must employ cautionary measures to limit contamination issues.

In analyzing the average analysis times of Tables 2–4, a final trend shows that the HP method requires twice the analysis time that is required by the UHP method. The UP method requires 1.5 times the analysis time that is required by the UHP method. It is clear to see that one can optimize the wet chemical oxidation efficiency by combining ultraviolet light, heat, and persulfate into one single instrument. The TOC-V_W Wet Chemical TOC analyzer provides better accuracy, faster analysis time, and reduced persulfate consumption by incorporation of the UHP method.

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