Reagentless (Ozone) Oxidation of Organics in Water

by
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The following discussion includes excerpts from historical reports on the theory and performance of reagentless UV oxidation used in the Astro ultraTOC on-line process monitor. The ultraTOC is the commercial version of NASA's TOC process control water quality monitor developed in the 1990s for zero-g operation on the space station.

UV/Persulfate Oxidation

A STANDARD METHOD for analyzing TOC is persulfate oxidation activated by UV irradiation (presented here as the reference method). Reagent-supported oxidation occurs when the persulfate ion is dissociated to produce hydroxyl radical (OH*), a very strong oxidizing agent. Organic carbon is oxidized to CO_2 via the following chemical reactions:

Solution

$$Na_2S_2O_8 \xrightarrow{H_20} 2Na^+ + S_2O_8^{-2}$$

Free Radical Generation

$$S_2O_8^{-2} + 2\,H_20 \xrightarrow[Heat]{UV} 2\,SO_4^{-2} + 2H^+ + 2OH^*$$

Hydrocarbon Oxidation

$$C_nH_m + (4n + m)[OH^*] \xrightarrow[Heat]{UV} nCO_2 + (2n + m)H_2O$$

UltraTOC Reagentless UV Oxidation

The combination of UV and ozone is highly effective in oxidizing organic materials in water. The mechanism seems to be a photosensitized oxidation process in which the contaminant molecules are excited and/or dissociated by the absorption of short-wavelength UV light. Simultaneously, hydroxyl radical is generated when molecular oxygen is dissociated and when ozone is dissociated by the absorption of short and long wavelengths of radiation. It was shown that this combination of UV and ozone oxidized contaminants 200 to 2,000 times faster than UV light alone or ozone alone. For maximum effectiveness, the sample was located within 5 mm of the UV source.

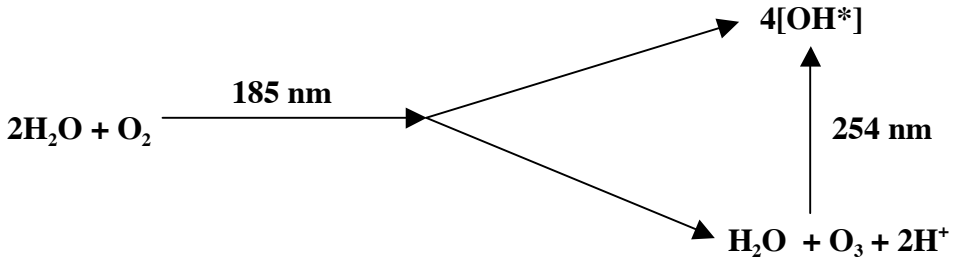
Free Radical Generation by absorption of 185 nm UV energy

$$2H_2O + O_2 \xrightarrow{185\ nm} H_2O + O_3 + 2H^+ \longleftrightarrow 4[OH^*]$$

Additionally, excess O_3 is decomposed by absorption of 254 nm UV energy

$$H_2O + O_3 + 2H^+ \xrightarrow{254\ nm} H_2O_2 + O_2 + 2H^+ \longleftrightarrow 4[OH^*]$$

Thus, oxidant is produced by the following paths



Hydrocarbon oxidation

$$C_nH_m + (4n + m)[OH^*] \longrightarrow nCO_2 + (2n + m)H_2O$$

Low-pressure mercury discharge lamps with high-quality glass envelopes generate the two wavelengths needed to accomplish this process: 184.9 nm and 253.7 nm. The 185 nm wavelength is important because it is absorbed by O_2, thereby leading to the generation of ozone. The 254 nm radiation is not absorbed by O_2, but is absorbed by most organics and by ozone. Thus, when both wavelengths are present, ozone is continually being formed and destroyed. An intermediate product, both of the formation and of the destruction processes, is hydroxyl radical.

The ultraTOC reactor design uses a low-pressure mercury lamp with a Suprasil envelope, configured for close contact of sample and the source envelope. Suprasil glass exhibits superior performance with a light attenuation of 8 % from 180 nm to the near infrared, as compared to ordinary fuzed quartz which attenuates UV energy by 10 % at 255 nm and 30 % at 185 nm. The 90 cm lamp is bent to form a flat grid and provides 100 mw/cm^2 at 254 nm and 10 mw/cm^2 at 185 nm. Two identical liquid-carrying grids are placed on each side of the lamp. Volume of each sample tube is 2.8 cc giving a total volume of 5.6 cc. The lamp with sample flow tubes is illustrated below.

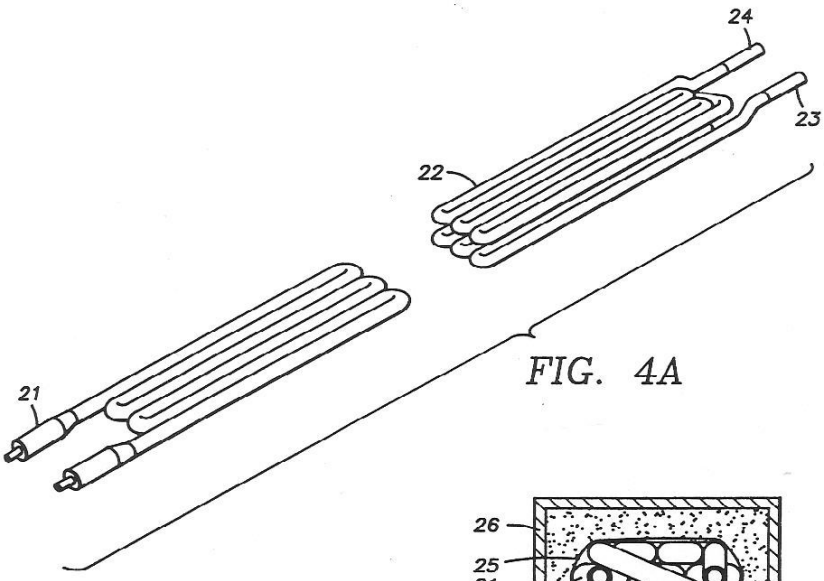


FIG. 4A

FIG. 4D

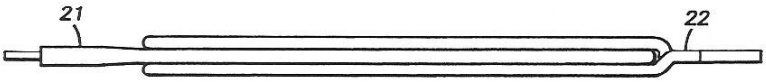


FIG. 4B

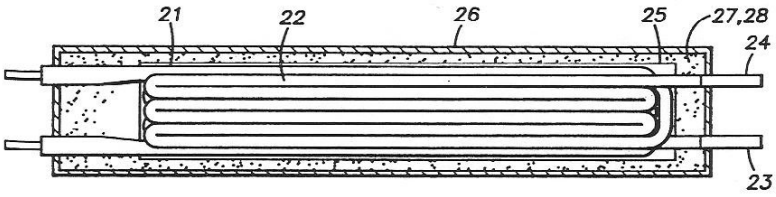


FIG. 4C

On average, 4 mg O_2 per mg TOC is stoichiometrically required to oxidize mixtures containing typical organic pollutants in manned spacecraft water. Thus, water saturated with O_2 (~40 mg/l) will oxidize as much as 10 mg/l TOC. The sample to the reactor is saturated with O_2, which is introduced upstream via the TIC/GLS O_2 purge. Samples which contain more than 10 mg/l require additional O_2 which could be provided by a mid-reactor membrane O_2 saturator connected serially between the two reactor sample tubes. Thus, as much as 10 mgC/l could be oxidized in each of the sample tubes for a total capacity of 20 mgC/l. Higher capacities would require additional reactors.

Reactor sizes ranging from 30 cm to 90 cm have been tested to determine performance effects of key parameters: total energy, sample distance from lamp, residence time, glass quality, and total O_2 supplied. Results for the three top candidates from these tests are summarized below, which shows high oxidation efficiency of KHP (potassium hydrogen phlalate), urea and methanol, both individually and in combination. The 90 cm lamp with 5.6 cc volume was selected for the ultraTOC design.

This reactor configuration differs from the typical commercial UV/Persulfate reactor, which usually consists of a tubular lamp inserted into a slightly larger-diameter tubular container, where water sample flows along the cylindrical annulus from inlet to exit ports. More recent tests showed that the commercial configuration (annulus irradiation) could be substituted in the ultraTOC for reagentless operation when improved to include Suprasil glass for the lamp, and with adequate residence time.

UltraTOC Reactor Oxidation of Urea

Residence Time, min.	Influent Conc mgC/l	Carbon Oxidized, % 60 cm mirrored 5.6cc 2.4mm by 4mm	90 cm 5.6cc 2mm by 3mm	90 cm 8.4cc 2.4mm by 4mm
1.8	1.0		87	
2.3	1.0		90	
4.3	1.0		99	
1.0	1.0		53**	
1.2	1.0		56**	
2.2	1.0		75**	
1.8	2.0	-	90	-
1.8	2.0*	-	75	-
2.8	2.0	-	95	-
2.8	2.0*	-	90	-
5.6	2.0	-	95	-
5.6	2.0*	-	90	-
2.1	5.0	-	-	78
2.8	5.0	78	92	-
4.2	5.0	-	-	96
4.2	5.0	-	-	74
5.6	5.0	80	92	-
8.4	5.0	-	-	92
8.4	5.0	-	-	94
11.2	5.0	94	90	-
16.8	5.0	-	-	94
2.8	10.0	53	73	-
4.2	10.0	-	-	77
	10.0	-	-	73
5.6	10.0	53	88	-
8.4	10.0	-	-	82
	10.0	-	-	73
11.2	10.0	-	88	-
16.8	10.0	-	-	87
2.8	20.0	43	47	-
4.2	20.0	-	-	39
5.6	20.0	43	64	-
8.4	20.0	-	-	53
11.2	20.0	-	61	-
16.8	20.0	-	-	53

without mid-reactor O2 saturator

* with 2 mg/l Iodine (as I)

** with 1 of 2 glass sample flow tubes removed

UltraTOC Reactor Oxidation of KHP

Residence Time, min.	Influent Conc mgC/l	Carbon Oxidized, % 60 cm mirrored 5.6cc 2.4mm by 4mm	90 cm 5.6cc 2mm by 3mm	90 cm 8.4cc 2.4mm by 4mm
0.8	0.20	-	100**	-
1.2	0.20	-	100**	-
2.2	0.20	-	100**	-
1.8	2.0	-	100	-
1.8	2.0*	-	100	-
2.8	2.0	100	100	-
2.8	2.0*	-	100	-
4.2	2.0	-	-	100
5.6	2.0	100	100	-
5.6	2.0*	-	100	-
8.4	2.0	-	-	100
2.8	5.0	92	96	
4.2	5.0			92
5.6	5.0	92	98	
8.4	5.0			92
0.8	10.0	96	-	-
1.1	10.0	93	-	-
1.4	10.0	98	99	-
2.1	10.0	-	-	98
2.8	10.0	99	99	-
2.8	10.0	-	98	-
4.2	10.0	-	-	99
4.2	10.0	-	-	97
5.6	10.0	-	98	-
8.4	10.0	-	-	98
1.4	20.0	73	79	-
2.8	20.0	98	99	-
2.8	20.0	73	75	-
5.6	20.0	99	100	-
5.6	20.0	71	-	-
11.2	20.0	99	-	-

without mid-reactor O2 saturator

* with 2 mg/l Iodine (as I)

** with 1 of 2 glass sample flow tubes removed

UltraTOC Reactor Oxidation of Methanol

Residence Time, min.	Influent Conc mgC/l	Carbon Oxidized, % 60 cm mirrored 5.6cc 2.4mm by 4mm	90 cm 5.6cc 2mm by 3mm	90 cm 8.4cc 2.4mm by 4mm
1.8	2.0	-	90	-
1.8	2.0*	-	95	-
2.8	2.0	-	100	-
2.8	2.0*	-	100	-
5.6	2.0	-	100	-
5.6	2.0*	-	100	-
2.8	5.0	-	100	-
5.6	5.0	-	100	-
1.4	10.0	-	92	-
2.8	10.0	99	99	-
2.8	10.0	-	90	-
5.6	10.0	99	98	-
5.6	10.0	-	79	-
11.2	10.0	95	95	-
1.4	20.0	-	49	-
2.8	20.0	61	82	-
2.8	20.0	-	51	-
4.2	20.0	-	-	64
5.6	20.0	52	75	-
5.6	20.0	-	41	-
11.2	20.0	58	93	-

* without mid-reactor O2 saturator
with 2 mg/l Iodine (as I)

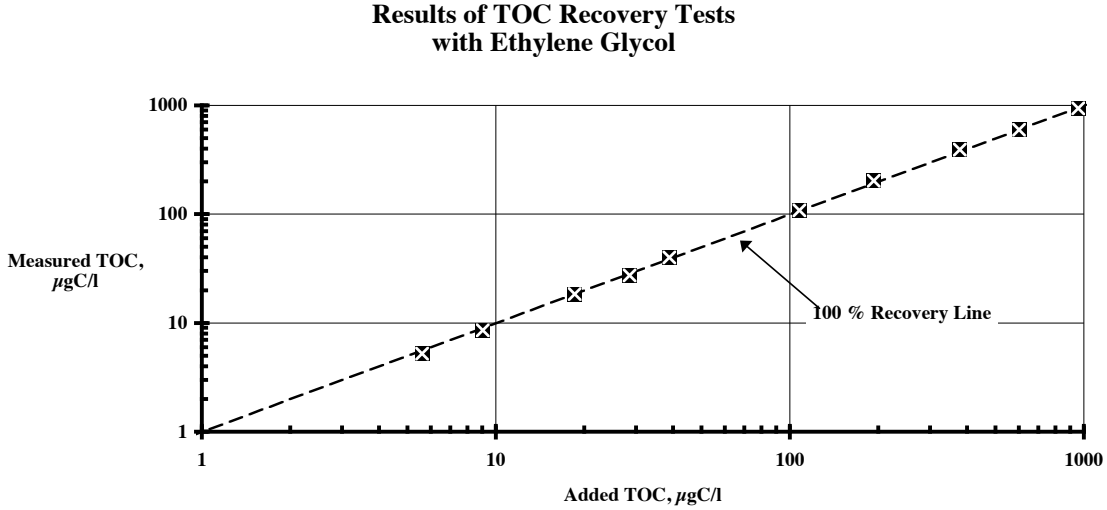
UltraTOC Reactor Oxidation of Ersatz
(1/3 each Urea, KHP, Methanol)

		Carbon Oxidized, %		
Residence Time, min.	Influent Conc mgC/l	60 cm mirrored 5.6cc 2.4mm by 4mm	90 cm 5.6cc 2mm by 3mm	90 cm 8.4cc 2.4mm by 4mm
1.8	2.0	-	95	-
1.8	2.0*	-	90	-
2.8	2.0	-	100	-
2.8	2.0*	-	100	-
5.6	2.0	-	100	-
5.6	2.0*	-	100	-
2.8	5.0	88	96	-
4.2	5.0	-	-	94
5.6	5.0	86	96	-
8.4	5.0	-	-	92
11.2	5.0	80	90	-
16.8	5.0	-	-	88
2.8	10.0	94	96	-
4.2	10.0	-	-	96
5.6	10.0	93	95	-
8.4	10.0	-	-	97
11.2	10.0	92	94	-
16.8	10.0	-	-	97
2.8	20.0	86	90	-
4.2	20.0	-	-	93
5.6	20.0	86	98	-
11.2	20.0	88	99	-
16.8	20.0	-	-	95

without mid-reactor O2 saturator

* with 2 mg/l Iodine (as I)

The chart below illustrates typical results of TOC-added tests showing linearity of the ultraTOC instrument.



Recoveries of various compounds for each of the ultraTOC operating modes - i.e.,Standard Mode at 2.1 cc/min (residence time 2.7 minutes); Medium Mode at 3.8 c/min (residence time 1.5 minutes); Turbo Mode at 7.5 cc/min (residence time 0.75 minutes) - are presented in the enclosed file, Recovery of Organics.xls.

The following are concluded from the above data:

1. Intensity and residence time of water sample exposure to 185 nm energy are most important to complete reagentless oxidation.
2. Only the more readily available 254 nm energy is required for oxidation with persulfate.
3. Reagentless oxidation can be equally effective given sufficient residence time. Observed lower recoveries of reagentless oxidation may be attributable to a slower reaction rate of hydroxyl radical generation from dissolved oxygen which depends on gas diffusion, compared to the generation rate which depends on ionic diffusion of S_2O_8.
4. Either reactor configuration, i.e., sandwich or annulus, is acceptable for reagentless oxidation.

References

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5. Jeffers, E.L., "Method for Reagentless Measurement of the Total Organic Carbon Content of an Aqueous Sample", U.S. Patent 5,672,516.

6. Donovan R.P., “Evaluation of On-Line TOC Analyzers for Monitoring Recycled Water in Semiconductor Processing, Part 1”, Article #UP 160228, Ultrapure Water Journal, February 1999.

7. Donovan R.P., “Evaluation of On-Line TOC Analyzers for Monitoring Recycled Water in Semiconductor Processing, Part 2”, Article #UP 160339, Ultrapure Water Journal, March 1999.