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# INTERNATIONAL OZONE Titan 4000 PERFORMANCE TESTING

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## Executive Summary

Hydroxyl (·OH) generators are designed to purify the environment in which they are operated. The general principle of operation is the oxidation of ambient water vapor using an ultra-violet (UV) lamp source to produce hydroxyl molecules, $\cdot OH$, also referred to in the industry and in the literature as hydroxyl radicals or hydroxyls. In ambient air, there are other reaction steps involving oxygen that contribute to the formation of hydroxyls, but the overall result is as shown below.

$$H_2O + hv \rightarrow H + \cdot OH$$

There are two main categories of hydroxyl generators. Those that use a broad spectrum of ultra-violet radiation to interact with water and oxygen in air; and those that use a single wavelength of ultra-violet light to shine on a photo catalytic surface. The latter method is often referred to as the Photo Catalytic Oxidation (PCO) method. Some generators combine these methods.

The International Ozone Titan 4000 air cleansing system is labeled and marketed as a hydroxyl generator. The Titan 4000 oxidizes compounds on the surface of a titanium dioxide ($TiO_2$) coated mesh which is illuminated by ultraviolet lamps, and all the reactions take place on the catalyst surface. Water and $O_2$ from the ambient atmosphere are adsorbed on the $TiO_2$ surface, which the reactant encounters upon flowing through the device. Hydroxyl radicals and super oxide ions ($O_2^-$) are produced directly on the catalyst surface after irradiation with 385 nm light. These oxidants react with organic reactants that are also adsorbed on the surface. Thus all of the reaction for the Titan 4000 system occurs on the $TiO_2$ catalyst surface, and no reactive hydroxyl radicals are ever ejected into the room or even into the gas phase portion of the reaction chamber according to the scientific literature.[5] This method is innately limited by the available surface area of the catalyst, which diminishes over time due to carbonization and contamination. It was intended to treat small volumes of air.

Little if any scientific data is available on the hydroxyl formation rate using either method. This is likely due to the fact that to do so accurately, it is necessary to use a specially designed test chamber. Hydroxyl free radicals are so reactive and short-lived that they cannot be practically measured directly by analytical methods in a laboratory. [1-5] An industry standard laboratory method for measuring hydroxyls is to measure the rate of removal of a specified amount of a volatile hydrocarbon (shown below as R-CH3) in an ultra-clean room environment under highly controlled conditions.[1] The hydrocarbon is chosen based on its ability to selectively react with only hydroxyl radicals and not other oxidants, such as ozone, that may be produced by UV photolysis of water vapor.

Because of the high level of reactivity of the hydroxyls, a special reaction chamber made of Teflon must be used to avoid loss of reactant from adsorption and reaction on chamber surfaces. The chamber must also be specially treated to remove all ambient organic and inorganic molecules using special filters and ventilation. Only then can the selected hydrocarbon reactant concentration changes be accurately measured and attributable solely to the formation and reaction of hydroxyls. Using this methodology, formation rates of hydroxyls as low as a few part per billion (ppb) have been routinely measured.

This experimental method was used to measure the hydroxyl formation rate for the Titan 4000, serial number TZ-12291, (International Ozone, Lantana, Florida 33462). The experiments involved the use of n-heptane, and 2-methyl-furan which selectively react with hydroxyls and not other oxidants that could be produced by the system. There is an abundance of data in the literature describing the kinetics and high rates of reaction of hydroxyls with these hydrocarbons to further enable confirmation that the reactions are due to the presence of hydroxyls.[1-5]

The test chamber was purged and the Titan 4000 was placed inside. The chamber was sealed and allowed to purge again so that a stable baseline was obtained. A sample of n-heptane was introduced into the system such that an initial vapor phase concentration of 0.13 ppb was obtained. The Titan 4000 was run for two hours, during which time the concentration of n-heptane was measured every few seconds by a gas chromatograph-mass spectrometer (GC-MS). No reduction in the concentration of n-heptane was measured, indicating that no measurable amount of hydroxyls was being formed. If any hydroxyls were formed they were below the 2-3 ppb sensitivity level of the GC-MS.

In an effort to determine if even low ppb of hydroxyls were being produced by the Titan 4000 system, the test was repeated using 2-methyl furan, a hydrocarbon that reacts twice as fast with hydroxyls as n-heptane and would therefore be twice as sensitive. Again, there was no verifiable concentration of hydroxyls produced by the Titan system during two hours of operation.

**In summary, under highly controlled conditions, there was no evidence that the Titan 4000 was producing hydroxyls using published analytical methods capable of measuring hydroxyl concentrations as low as 2-5 ppb.**

## Materials and Methods

The experiments described here were conducted in a 120 cubic meter (120,000 liters) Teflon chamber. The walls and floor are made of inert “water-clear” Teflon film. A high-volume ventilation fan connected to a HEPA filter removes particulate material from ambient air during large-volume flushing of the chamber. A clean air generator scrubs moisture, VOCs and particulate material from air before it enters the chamber. The chamber contents are monitored continuously via sample lines that pass through the floor of the chamber and into the laboratory. Gas chromatography was conducted on the purged chamber and showed little background compounds that could interfere with the tests. The experiments were conducted at night so no sunlight would cause photochemical oxidation of the test mixtures. For all experiments, the Titan 4000 was placed inside the chamber in the middle of the floor; a heavy duty electrical power extension cord passed through a small opening in the floor to the outside to allow for remote powering and operation. Power and operation was confirmed by visual observation of the green power light and hearing the blower. Two mixing fans, one each at both ends of the chamber, were turned on to assure complete mixing. All experiments were conducted with addition of a low concentration of an inert non-reactive dilution tracer of carbon tetrachloride (2.5 micro-liters in the chamber). Since several continuous monitoring instruments are sampling from the chamber continuously, the chamber contents are diluted about 1-2 percent per hour, which is considered low. The measurement of the dilution tracer shows this steady slow decrease in concentration. Any compounds that are not reacting would decrease in relative concentration equal to this dilution rate, and any chemical reactivity with ·OH would cause a larger decrease in concentration. All other air pollutant measurements are compared and corrected using these dilution measurements.

## Results

### Hydrocarbon Removal (Heptane Treatment)

A sample of n-heptane was injected into the chamber such that the concentration was 0.13 ppmV. The n-heptane concentration was monitored to establish initial test conditions and demonstrate stability before operation of the hydroxyl generators. All data presented in this report are corrected for dilution using the monitored tracer (carbon tetrachloride). The background air was measured with gas chromatography and mass spectrometry and was observed to be clean, i.e. there were no organic compounds present above 1-2 ppb.

The Titan unit was powered on at 1929 (7:29 PM) and was operated for 2 hours. During this time the n-heptane concentration was monitored and showed no decrease in concentration with the decay rate shown as a regression slope in ppm per hour (Figure 1). It can be concluded that there was no observable n-heptane decay when the unit was operational.

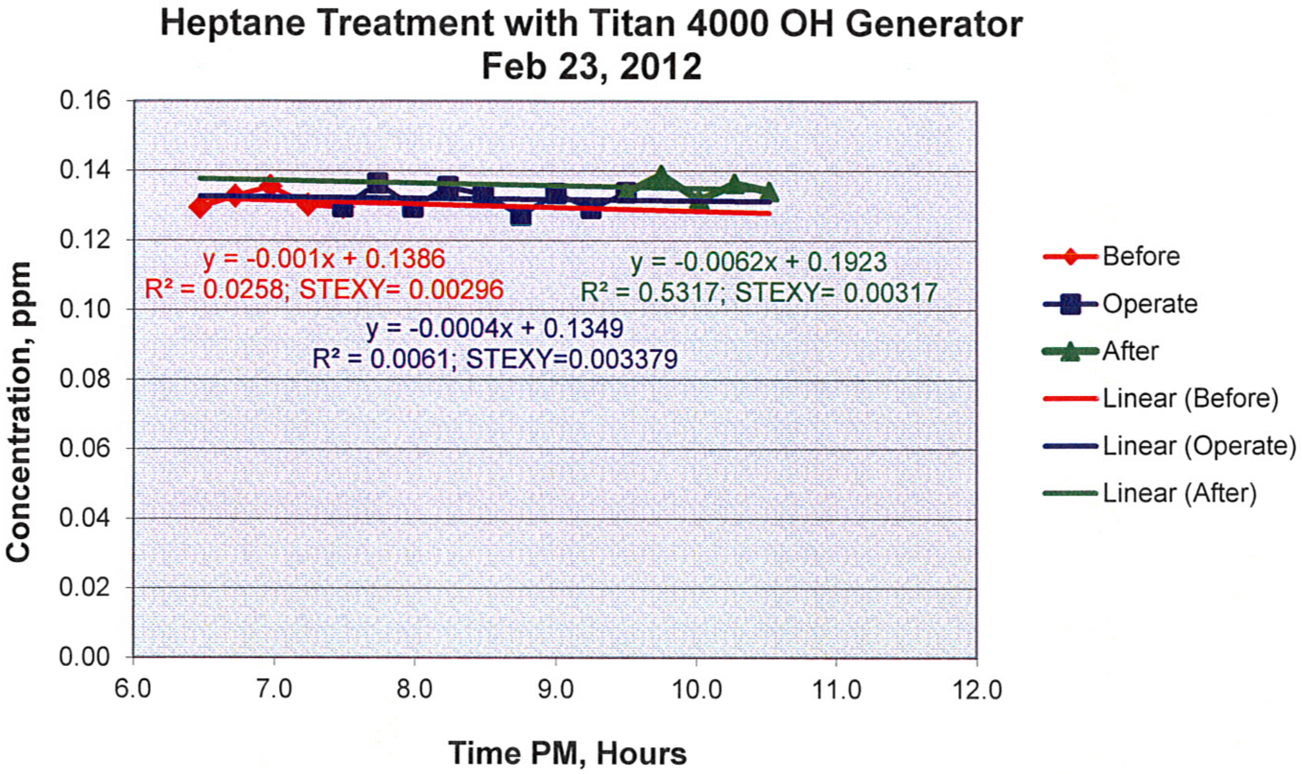

**Figure 1 Heptane treatment, Titan 4000 hydroxyl generator.**

## Hydrocarbon Removal (2-methyl-Furan Treatment)

The experiment was repeated with 2-methy-furan, a hydrocarbon which reacts twice as fast with hydroxyls compared with n-heptane to increase the opportunity to detect hydroxyl formation. The Titan unit was powered on at 2034 (8:34 PM) and was operated for 2 hours. During this time the 2-methyl-furan was monitored and showed no decrease in concentration with the decay rate shown as a regression, slope in ppm per hour (Figure 2). It can be concluded that there was no observable 2-methyl-furan decay when the unit was operational.

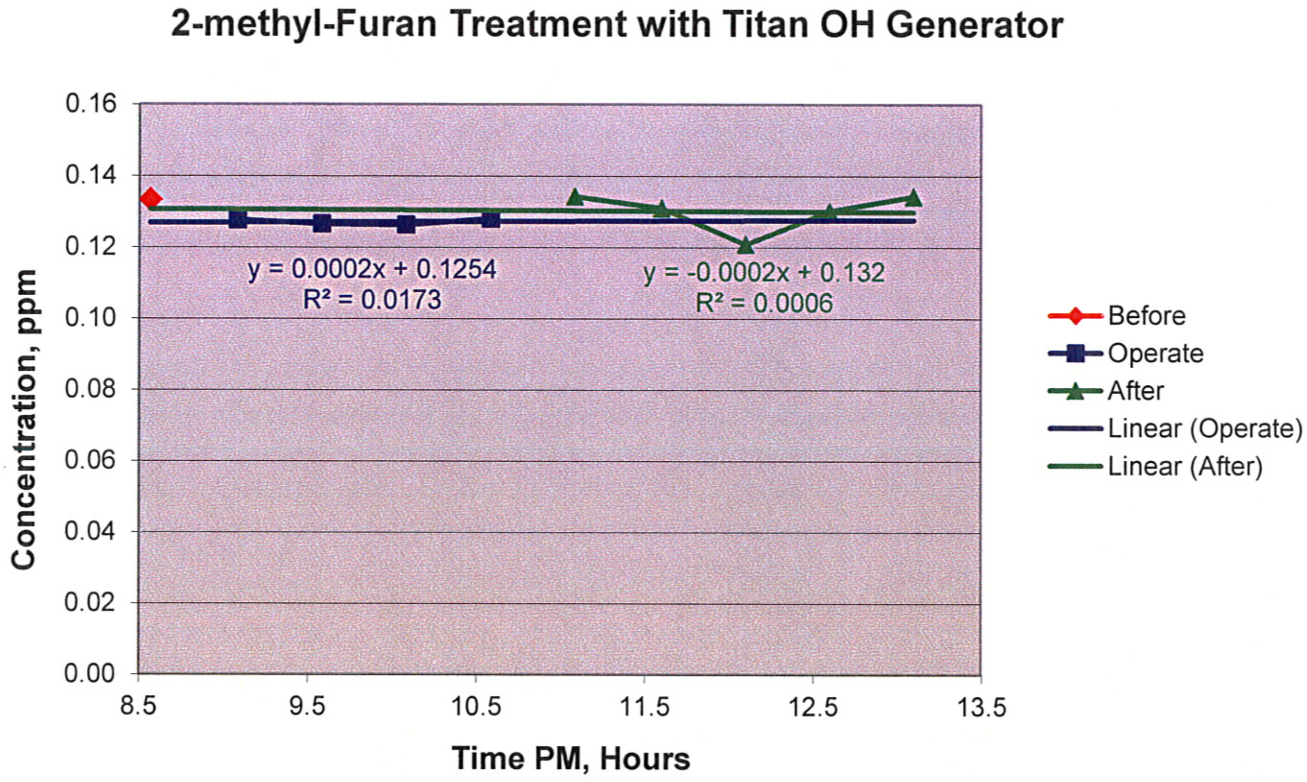

**Figure 2** **2-methyl-Furan treatment, Titan 4000 hydroxyl generator.**

### References

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2. B. J. Finlayson Pitts and J. N. Pitts, Jr., *The Chemistry of the Upper and Lower Atmosphere*, Academic Press, San Diego, 1999.
3. C. J. Weschler and H. C. Shields, Production of the Hydroxyl Radical in Indoor Air, Environ. Sci. Tech. **30**, 3250 (1996).
4. W. B. Demore et al., *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*, NASA Report JPL 97-4, 1997.
5. W. A. Jacoby, D. M. Blake, J. A. Fennell, J. E. Boulter, L. M. Vargo, M. C. George, and S. K. Dolberg, Heterogeneous Photocatalysis for Control of Volatile Organic Compounds in Indoor Air, J. Air. Waste Mgmt. Assocn. **46**, 891 (1996).

# Appendix

## Test Condition Summary for the Hydroxyl Generator Experiments

**Operating Conditions**

***Titan Heptane Treatment Feb 23, 2012***

1745 stop venting; insert Titan
1804 start Chars\tscan
1818 4 ul CCL4 injected
1819 95 ul Heptane injected; cham temp 293.2K; DP is 11.8C
1828 first GC of heptane
1846 ccl4 first gc
1929 Start power
Titan
2129 stop power Titan

**Heptane Decay**

| | ppm | ppm | ppm |
|---|---|---|---|
| Time Hours | Before | Operate | After |
| 6:28 PM | 0.129439 | | |
| 6:43 PM | 0.132694 | | |
| 6:58 PM | 0.135423 | | |
| 7:14 PM | 0.130143 | | |
| 7:29 PM | 0.129477 | | |
| 7:29 PM | | 0.12947703 | |
| 7:44 PM | | 0.13633888 | |
| 7:59 PM | | 0.12943818 | |
| 8:14 PM | | 0.13530948 | |
| 8:29 PM | | 0.1331505 | |
| 8:45 PM | | 0.12713729 | |
| 9:00 PM | | 0.13338526 | |
| 9:15 PM | | 0.12913448 | |
| 9:30 PM | | 0.13364741 | |
| 9:30 PM | | | 0.133647 |
| 9:45 PM | | | 0.138777 |
| 10:01 PM | | | 0.131536 |
| 10:16 PM | | | 0.136257 |
| 10:31 PM | | | 0.133982 |

**Operating Conditions**

***Titan 2-methyl-furan Treatment Oct 05, 2011***

2034 Start power Titan
2235 stop power Titan

| | 2-methyl-furan Decay | | | Ozone Production | | Formaldehyde Production | |
|---|---|---|---|---|---|---|---|
| | ppm | ppm | ppm | | | | |
| Time | Before | Operate | After | Time Hours | O3 ppm | Time Hours | HCHO ppm |
| 8:34 PM | 0.133356 | | | no data | | Not detected | |
| 8:34 PM | 0.133356 | | | | | | |
| 9:05 PM | | 0.127629 | | | | | |
| 9:35 PM | | 0.126507 | | | | | |
| 10:05 PM | | 0.126258 | | | | | |
| 10:35 PM | | 0.127999 | | | | | |
| 11:05 PM | | | 0.13418 | | | | |
| 11:36 PM | | | 0.130883 | | | | |
| 12:06 AM | | | 0.120732 | | | | |
| 12:36 AM | | | 0.130068 | | | | |
| 1:06 AM | | | 0.134236 | | | | |