

Puraclenz P3000 VOC Challenge Gas Testing and Byproduct Analysis

Summary: Due to the increasing concerns over indoor air quality, many different approaches to air purification have made their way into the marketplace. As a means of better understanding the effects of Puraclenz's Advanced Photocatalytic Oxidation (PCO) technology, the Puraclenz P3000 device was tested against three common Volatile Organic Compounds (VOCs) and their interaction with the Puraclenz technology was monitored in real-time via mass spectrometry. These three compounds and their corresponding levels were chosen based on internationally recognized VOC testing protocol NRCC-54013. This report summarizes the findings of two different challenge gas tests for the P3000 device as follows.

1. The first test conducted in a 30 m³ stainless steel chamber includes data reported by RJ Lee Group and Intertek related to a 24-hour testing that occurred based on NRCC-54013 Section 5.1.2 (2011), ISO 16000-3 (2011), and ISO16000-6 (2011) at Intertek's Kentwood, MI, laboratory. RJ Lee and Intertek worked in conjunction to conduct this test.
2. The second test conducted in 1 m³ Teflon chamber includes data reported by RJ Lee Group on a subsequent 4-hour challenge gas test conducted to answer questions related to methanol and acetonitrile levels measured in the first test related to chemicals used to clean the 30 m³ stainless steel chamber before the first test was conducted.
3. A comparison between the two studies is presented at the end of the report.
4. The concentrations of the compounds generated during the oxidation of the gases from the P3000 device were compared to the OSHA permissible exposure limits (PEL).

Methods: Challenge-gas studies were performed in 30 m³ stainless steel chamber and in a 1 m³ Teflon chamber containing an P3000 electronic air purifier. The compounds formaldehyde, D-limonene and toluene were injected into the chamber as challenged gases. Both first and second tests used Mass Spectrometers that measure VOCs in real time at 1 second increments for 24 hour and 4 hour periods respectively. The Proton Transfer Reaction Mass Spectrometer (PTR-MS) (PTR-TOF 4000, Ionicon, Innsbruck, Austria) was implemented for the real time monitoring of multiple VOCs. Furthermore, a DustTrak particulate monitor provided measurements of mass concentration of particulate at PM1, PM2.5 and PM10 to determine if the P3000 device generated particulate byproducts during the PCO reaction. A Thermal Desorption Gas Chromatography Mass Spectrometer (TD/GC-MS) and a High-Performance Liquid Chromatograph (HPLC) were used. During the first test, air samples were collected with sorbent tubes for the TD/GC-MS and HPLC. Ion counts were measured throughout both tests using a COM-Systems 3200-PRO Air Ion Counter.

The studies were conducted in compliance with the Quality Assurance practices and Quality Assurance Manual of the RJ Lee Group, Inc., which is compliant with the Laboratory's multiple national Accreditations, including ISO-17025.

Results: In the first test, after 24 hours of P3000 device operation toluene decreased by $61 \mu\text{g m}^{-3}$, D-limonene decreased by $120 \mu\text{g m}^{-3}$ and formaldehyde did not change during the 24-hour test. The second test did not detect elevated levels of methane and acetonitrile that were measured during the first test, which concludes that the first test measured introduced gasses used by Intertek from the sorption tube and impingement cleaning, and it can be concluded that these compounds were not created by the P3000 device. Other compounds such as ketones and aldehydes were registered during the test due to oxidation, but all compounds measured were at least 35 times lower than the OSHA permissible exposure limit (PEL). Finally, no particulate byproduct formation was noticed. In the first test trial, the average number of ambient ions measured in the test chamber was 800-1,000 ions/cm³.

Conclusions: The P3000 air purification device had a negligible effect on the formation of the number and type of VOCs as byproducts of the PCO reaction present in the chambers. The concentrations of VOCs that saw an increase were at least 35 times lower than the OSHA safe exposure limit, and many were below detectable limits. Finally, no particulate formation was noticed.

First challenge gas testing

PTR-ToF-MS Results

During the study conducted on 6/17/2021 a Puraclenz P3000 unit was exposed to 3 challenge gases using in a 30 m³ chamber at an Intertek facility. A Proton Transfer Reaction Mass Spectrometer model Ionicon PTR-TOF-MS-4000 (PTR-MS) was used for continuous monitoring of the volatile organic compounds. The data were generated in 1-second increments.

Test description: The P3000 unit was placed in a 30m³ testing chamber. The sampling started at 9:19 am. At 9:30 am three compounds (toluene, formaldehyde, limonene) were injected in the chamber. At 10:07 am the P3000 was turned on. The testing continued for 24 hours.

In total 55 compounds were identified by the PTR-MS data analysis. Table 1 summarizes the measurements of the three challenge gases (toluene, formaldehyde, limonene) as well as 4 noteworthy compounds. The table also includes the minimum detection limit per compound (MDL). The concentration of several compounds increased during the 24-hr experiment after the P3000 was turned on. Such compounds were methanol (0.11 ppm), acetaldehyde (0.004 ppm), acetonitrile (0.007 ppm), acetic acid (0.0004 ppm), propene (0.0002 ppm), ethanol (0.001 ppm), butadiene (0.002 ppm), butanol (0.003 ppm), isoprene (0.0004 ppm), pentene (0.0003 ppm), hexene (0.0002 ppm), cycloheptene (0.0002 ppm), C8 aromatics (0.0002 ppm) and heptanal (0.0005 ppm). As noted, all compounds that saw increase were several orders of magnitude lower than OSHA PELs.

Table 1: Mass concentration of the three challenge gases and 4 compounds of interest during different periods of the first challenge gas testing

Compounds of Interest		Formaldehyde	Methanol	Acetonitrile	Acetaldehyde	Acetone	Toluene	Limonene
MDL (ppm)		0.0006	0.002	0.004	0.005	0.001	0.0003	0.0001
Time	Description	Concentration (ppm)						
6/17/2021 9:22:05	Clean chamber	0.001	0.017	0.004	0.006	0.002	0.0005	0.002
6/17/2021 9:44:40	Max concentration of challenge gases	0.023	0.299	0.004	0.013	0.004	0.231	0.179
6/17/2021 10:07:00	P3000 is turned on	0.023	0.314	0.005	0.012	0.004	0.230	0.179
6/17/2021 14:07:00	4h operation of P3000	0.023	0.420	0.011	0.008	0.003	0.187	0.143
6/17/2021 18:07:00	8h operation of P3000	0.021	0.419	0.012	0.007	0.003	0.169	0.125
6/17/2021 22:07:00	12h operation of P3000	0.020	0.411	0.012	0.007	0.003	0.167	0.126
6/18/2021 2:07:00	16h operation of P3000	0.022	0.417	0.012	0.006	0.003	0.169	0.126
6/18/2021 6:07:00	20h operation of P3000	0.023	0.435	0.012	0.007	0.004	0.173	0.128
6/18/2021 10:07:00	24h operation of P3000	0.023	0.427	0.012	0.007	0.003	0.179	0.128

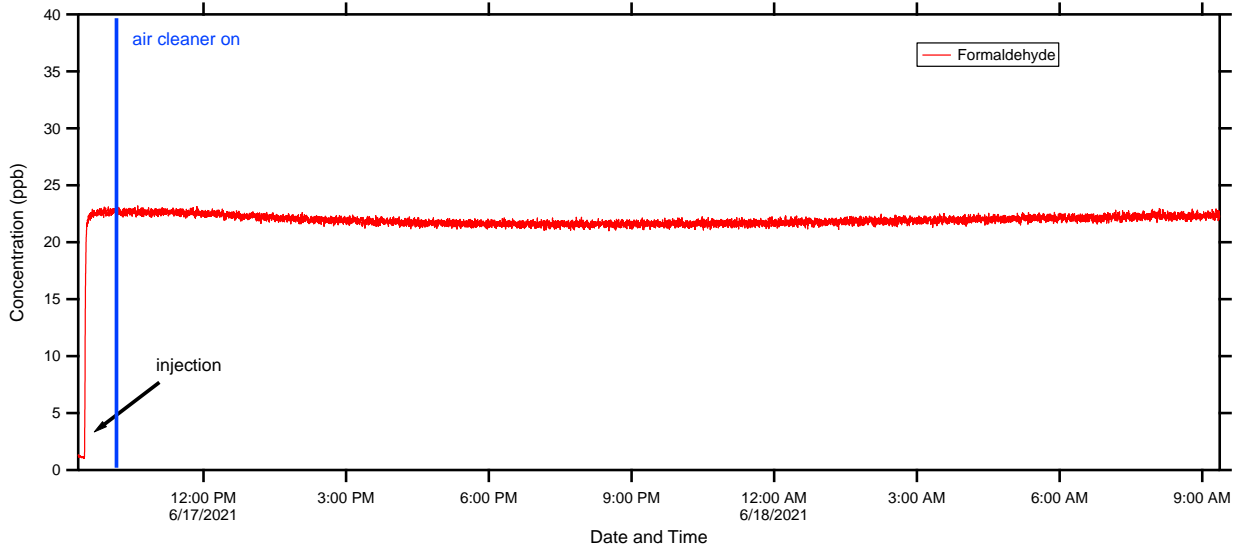


Figure 1: The mass spectrometry concentration time series of formaldehyde during 1st test. The time of the injection and the time in which the P3000 was turned on are also shown.

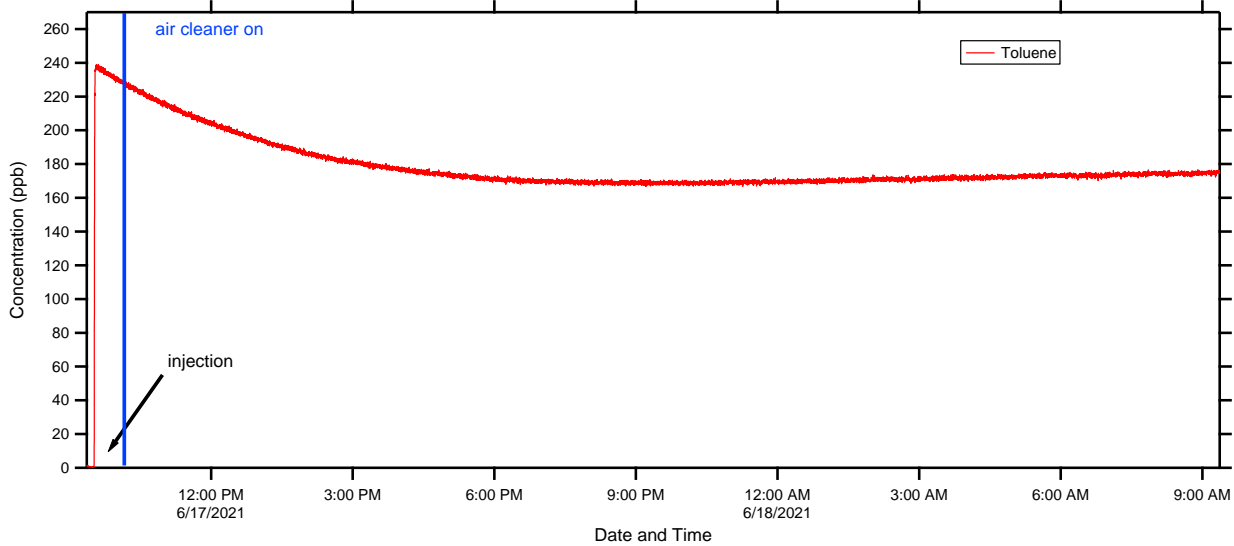


Figure 2: The mass spectrometry concentration time series of toluene during 1st test. The time of the injection and the time in which the P3000 was turned on are also shown.

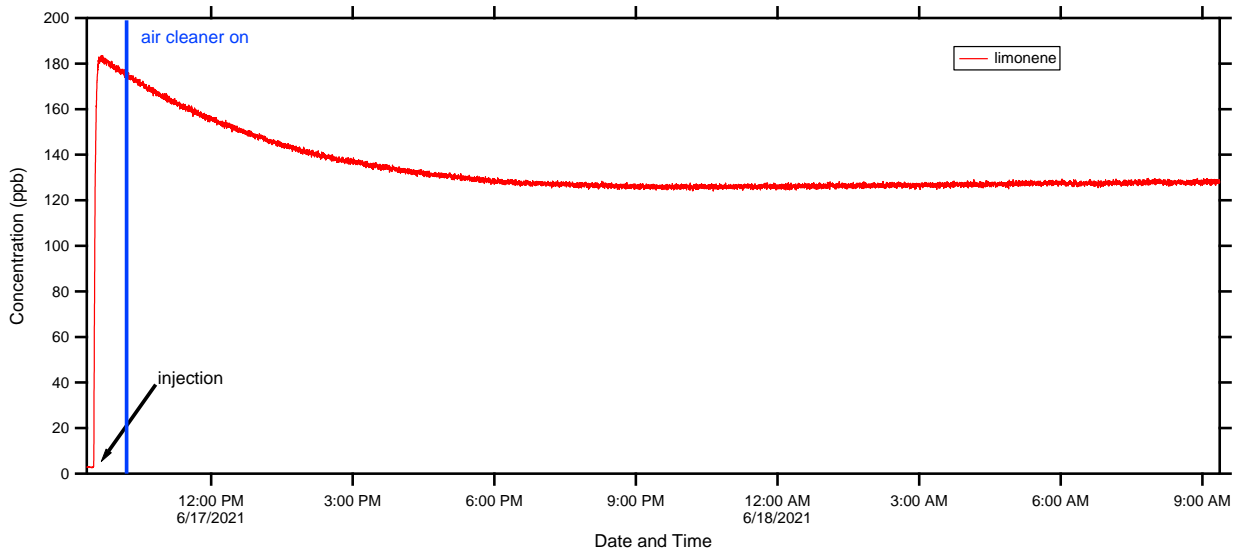


Figure 3: The mass concentration timeseries of limonene during 1st test. The time of the injection and the time in which the P3000 was turned on are also shown.

TD-GC/MS and HPLC results by Intertek

VOC samples were collected at 5, 10, 15, 20, 25, 30, 45, 60, 90, 120, 180, 240, 360, 480, and 1,440 minutes after starting the system. Samples analyzed for the challenge compounds were collected on multi-sorbent tubes containing Tenax TA. These VOC samples were analyzed by thermal desorption-gas chromatography/mass-spectroscopy, TD-GC/MS.

The analysis for potential byproducts focused on compounds smaller than C₁₀ (D-limonene). Multisorbent tubes containing Tenax TA® 35/60 and Carbograph 5 TD 40/60 are rated to retain compounds with

volatility between 1,3-butadiene to C20 including low molecular weight oxygenates, such as C2-C8 alcohols, C2-C8 carboxylic acids, and C3-C8 ketones. Air samples were analyzed by thermal desorption gas chromatography/mass-spectroscopy, TD-GC/MS (ISO 16000-6). Individual VOCs were calculated using toluene as a surrogate. Samples analyzed for low molecular weight aldehyde and ketones were collected on cartridges treated with 2,4-di-nitrophenylhydrazine (DNPH) and were analyzed using high performance liquid chromatography, HPLC (ISO 16000-3). Individual VOC concentrations were calculated using calibration curves based on pure standards. Detectable low molecular weight aldehyde and ketones include; acetaldehyde, acrolein, acetone, propionaldehyde, crotonaldehyde, methacrolein, n-butyraldehyde, benzaldehyde, valeraldehyde, m-tolualdehyde, and hexaldehyde.

Different compounds were also identified in lower concentrations. Acrolein, propionaldehyde, crotonaldehyde, methacrolein, n-butyraldehyde, benzaldehyde, valeraldehyde, m-tolualdehyde, and hexaldehyde had concentration lower than the instrument's detection limit, while acetone reached 0.005 ppm 24 hours after the P3000 device was turned on. Acetaldehyde was also 0.003 ppm 24 hours after the P3000 device was turned on. Benzene, 1-chloro4-(trifluoromethyl)-, xylene isomer, α -pinene and β -pinene were lower than 0.001 ppm during the testing.

Table 2 summarizes a direct comparison of the challenge gases between the different analytical techniques used. The biggest discrepancy in the two techniques was the concentration of formaldehyde. More specifically when the P3000 device was turned on the concentration of formaldehyde measured by the TD-GC/MS was $155 \mu\text{g m}^{-3}$ (0.126 ppm) while the corresponding concentration reported by the PTR-ToF-MS was $28.2 \mu\text{g m}^{-3}$ (0.023 ppm). The proton affinity of formaldehyde is very close to the proton affinity of water and there is always expected an underestimation of the concentration when the PTR-ToF-MS operates in H_3O^+ mode. The other two challenge gases; toluene and D-limonene had quite similar concentration.

According to the PTR-MS measurements, when the P3000 device was turned on, the concentration of acetone and acetaldehyde was 0.004 and 0.011 ppm respectively, while the corresponding reported concentrations measured by the TD-GC/MS were below the detection limit. 24 hours after the P3000 device was turned on, the acetone and acetaldehyde dropped to 0.003 and 0.007 ppm respectively according to the PTR-MS results, while the TD-GC/MS results showed that the corresponding concentrations were 0.005 and 0.003 ppm.

The differences on the measured concentration between the two different techniques lie on the principles of the techniques since the PTR-MS reported real-time measurements of the VOCs' concentration while the TD-GC/MS analysis is an off-line technique with samples that collected, stored and analyzed after the end of the testing. VOCs losses during sample collection and storing would likely be the main reason of the reported concentration differences.

Table 2. Comparison of challenge gases concentration between the two different techniques.

Compound	Formaldehyde ($\mu\text{g m}^{-3}$)		Toluene ($\mu\text{g m}^{-3}$)		D-Limonene ($\mu\text{g m}^{-3}$)	
	HPLC	PTR-MS	TD-GC/MS	PTR-MS	TD-GC/MS	PTR-MS
Measurement Technique						
Time after air cleaner turned on (min)						
0.0	155.0	28.2	763.0	867.5	770.0	997.5
5.0	151.0	27.6	742.0	877.4	769.0	992.6
10.0	154.0	26.6	761.0	852.2	768.0	977.8
15.0	149.0	26.8	756.0	844.5	792.0	964.3
20.0	152.0	27.7	750.0	834.1	764.0	953.6
25.0	155.0	27.6	759.0	846.7	787.0	959.9
30.0	153.0	28.1	741.0	839.4	765.0	967.5
45.0	149.0	28.3	747.0	810.8	754.0	910.0
60.0	155.0	27.2	733.0	812.2	711.0	925.6
90.0	154.0	28.2	746.0	791.5	758.0	898.8
120.0	151.0	27.5	757.0	763.9	748.0	872.1
180.0	150.0	26.4	739.0	754.8	726.0	822.6
240.0	148.0	27.4	740.0	705.3	720.0	797.9
360.0	155.0	28.2	729.0	663.8	707.0	728.7
480.0	153.0	26.3	724.0	628.7	699.0	697.6
1440 (24h)	153.0	27.9	702.0	658.2	650.0	723.3

Second challenge gas testing

An additional 4-hour challenge gas test took place using a 1m³ Teflon chamber. The purpose of the test was to investigate the existence of high concentrations of methanol and acetonitrile that were present in the first test done at the Intertek facility.

Test description: Similar to the first test toluene, limonene and formaldehyde were used injected to the chamber at 1:15 pm. Approximately 45 min later the P3000 device was turned on. The concentration of the compounds was 0.248 ppm of toluene, 0.152 ppm of limonene and 0.019 ppm of formaldehyde when the P3000 was turned on. Table 3 summarizes the concentration of the compounds of interest at several steps of the test. The concentration of limonene and toluene decreased. Formaldehyde was found to increase approximately 0.030 ppm in approximately 4 hours.

The 55 identified compounds from the first study were also measured during the second study. Compounds that were increased during the operation of the P3000 device included formaldehyde (0.023 ppm), methanol (0.040 ppm), acetaldehyde (0.040 ppm), acetic acid (0.020 ppm), propene (0.007 ppm), acetone (0.030 ppm), butadiene (0.011 ppm), butanol (0.066 ppm), benzene (0.008 ppm), C8 aromatics (0.034 ppm),

toluidine (0.007 ppm). In addition smaller increase was noticed in the following compounds: methyl ethyl ketone (0.007 ppm), heptanal (0.004 ppm), isoprene (0.004 ppm), formamide (0.004 ppm), methyl vinyl ketone (0.004 ppm), pentenes (0.002 ppm), hexene (0.003 ppm), hexenal (0.001 ppm), ethanol (0.002 ppm), acrylic acid (0.002 ppm), C4 thiols/sulfides (0.003 ppm), C5 carbonyl (0.003 ppm) and cycloheptene (0.002 ppm). Finally, only 0.0008 ppm of acetonitrile was produced.

Table 3: Mass concentration of the three challenge gases and 4 compounds of interest during different periods of the second challenge gas testing

Compounds of Interest	Formaldehyde	Methanol	Acetonitrile	Acetaldehyde	Acetone	Toluene	Limonene
MDL (ppm)	0.0004	0.0008	0.0001	0.0006	0.001	0.00	0.0002
Description	Concentration (ppm)						
Clean chamber	0.002	0.013	<MDL	0.004	<MDL	0.0003	<MDL
Max concentration of challenge gases	0.019	0.034	0.0003	0.008	<MDL	0.202	0.117
P3000 is turned on	0.016	0.031	0.0003	0.007	<MDL	0.176	0.118
1h operation of P3000	0.018	0.037	0.0004	0.014	0.005	0.158	0.098
2h operation of P3000	0.026	0.050	0.0005	0.026	0.015	0.169	0.097
3h operation of P3000	0.031	0.057	0.0007	0.035	0.021	0.174	0.097
3.75h operation of P3000	0.038	0.069	0.001	0.045	0.029	0.175	0.088

Comparison between the two studies

The final concentrations after four hours of testing methanol and acetonitrile concentrations were one order of magnitude lower than the first study at the Intertek facility. This confirms that the high levels of acetonitrile that were measured in the first study were not produced by the EAC but from the TO-11 cartridges. In addition, the high levels of methanol were not produced by the EAC, but they were introduced in the chamber during the injection. In between the injection of the compounds in the chamber the syringe was cleaned with methanol. During the second study the syringe was cleaned with hexane.

In addition, during this test higher production of aldehydes was measured than in the first challenge test. More specifically during the first test formaldehydes concentration decreased 0.0007 ppm while acetaldehyde had a concentration decrease of 0.004 ppm. However, during the second test formaldehyde increased by 0.021 ppm and acetaldehyde increased by 0.038 ppm. Aldehydes are expected to form during the oxidation of the sesquiterpenes (limonene) and aromatic compounds (toluene). A possible reason for the discrepancy is the difference between the size and type of chamber that was used between the two studies. The difference of material of the chamber can lead to the vapors loss rate on walls of the chamber.

In addition, the concentration of the ions released by the P3000 will be 30 times higher since the volume of the second chamber was approximately 30 times smaller than the first chamber. thereby dramatically increasing the VOC reactions.

Comparison with the OSHA permissible exposure limits (PEL)

Table 1 and Table 2 show the VOCs produced during the two tests and the corresponding OSHA exposure limits. The OSHA permissible exposure limits (PEL), were found in Tables Z-1, Z-2, and Z-3 of the OSHA General Industry Air Contaminants Standard (29 CFR 1910.1000), that were effective on July 1, 1993* and which are currently enforced by OSHA. TWA (time-weighted averaged) concentrations for OSHA PEL must not be exceeded during any 8-hour work shift of a 40-hour workweek. Most of the produced compounds were oxidation products. The compounds with the highest increase (>0.01ppm) during the tests were methanol, acetaldehyde, acetic acid, butanol, butadiene and C8 aromatics. The second test confirmed that the high concentrations of acetonitrile and methanol measured in the first chamber (first test) were produced from the sorbent tubes used for sample collection and not from the P3000 device. The results suggest that the VOCs produced during the P3000 device operation were at least 35 times lower than existing OSHA standards.

Table 4. Produced VOCs and OSHA exposure limits.

Compound	Produced after 4 hours of P3000 Device turned on			Produced after 24 hours of P3000 Device turned on		OSHA standard PEL-TWA (ppm)
	PTR-MS (1 st study) (ppm)	HPLC (1 st study) (ppm)	PTR-MS (2 nd study) (ppm)	PTR-MS (1 st study) (ppm)	HPLC (1 st study) (ppm)	
Formaldehyde	-	-	0.021	0.000	-	0.75
Methanol	0.106	-	0.038	0.113	-	200
Acetonitrile	0.006	-	0.001	0.007	-	40
Acetaldehyde	-	-	0.038	-	0.003	200
Acetone	-	0.004	0.028	-	0.005	1000
Toluene	-	-	-	-	-	10
Limonene	-	-	-	-	-	-

Table 5. Additional compounds produced during the first and the second tests. The reported data are from the PTR-MS measurements.

Compound	Produced after 4 hours of P300 Device turned on	Produced after 24 hours of P300 Device turned on	OSHA standard PEL-TWA (ppm)
	PTR-MS (2 nd study) (ppm)	PTR-MS (1 st study) (ppm)	
Acetic Acid	0.017	0.0004	10
Propene	0.0065	0.0002	100
Ethanol	0.0019	0.0014	1000
Butadiene	0.0114	0.002	1
Butanol	0.0661	0.0029	100
Isoprene	0.0044	0.0004	-
Pentene	0.0023	0.0003	-
Hexene	0.0025	0.0002	500
Cyclopentene	0.0015	0.0002	-
C8 Aromatics	0.034	0.0002	-
Heptanal	0.0037	0.0005	-
Benzene	0.0082	-	1
Toluidine	0.0072	-	5
Methyl Ethyl Ketone	0.0067	-	200
Formamide	0.0038	-	-
Methyl Vinyl Ketone	0.0035	-	-
Hexanal	0.0014	-	-
Acrylic Acid	0.0017	-	-
C4 thiols/sulfides	0.0028	-	-
C5 Carbonyl	0.0028	-	-

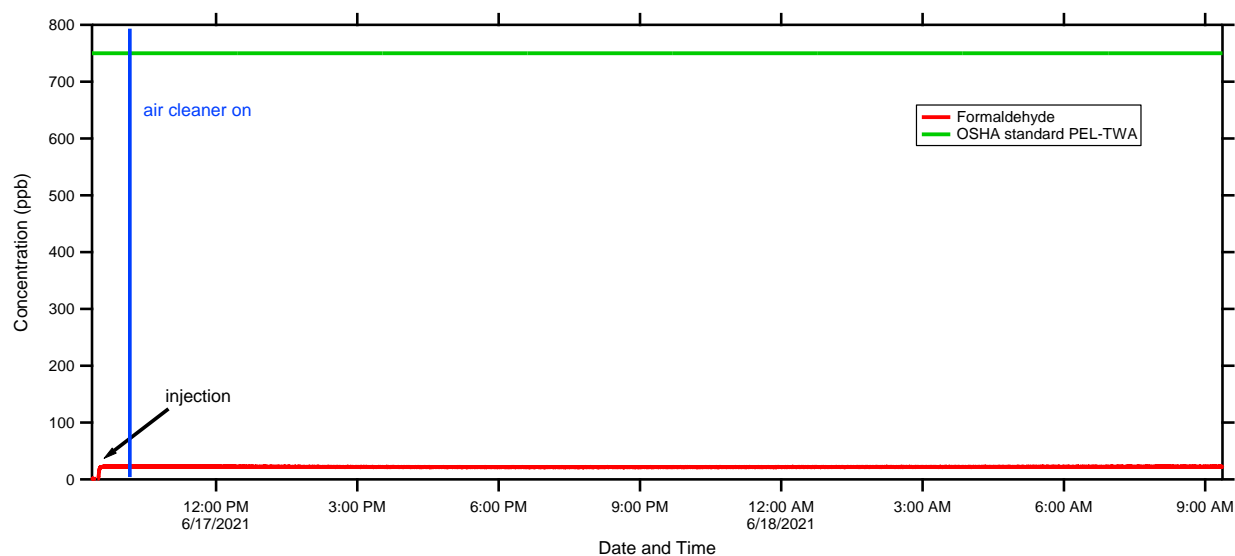


Figure 4. Formaldehyde timeseries during 1st test and OSHA standard PEL-TWA.

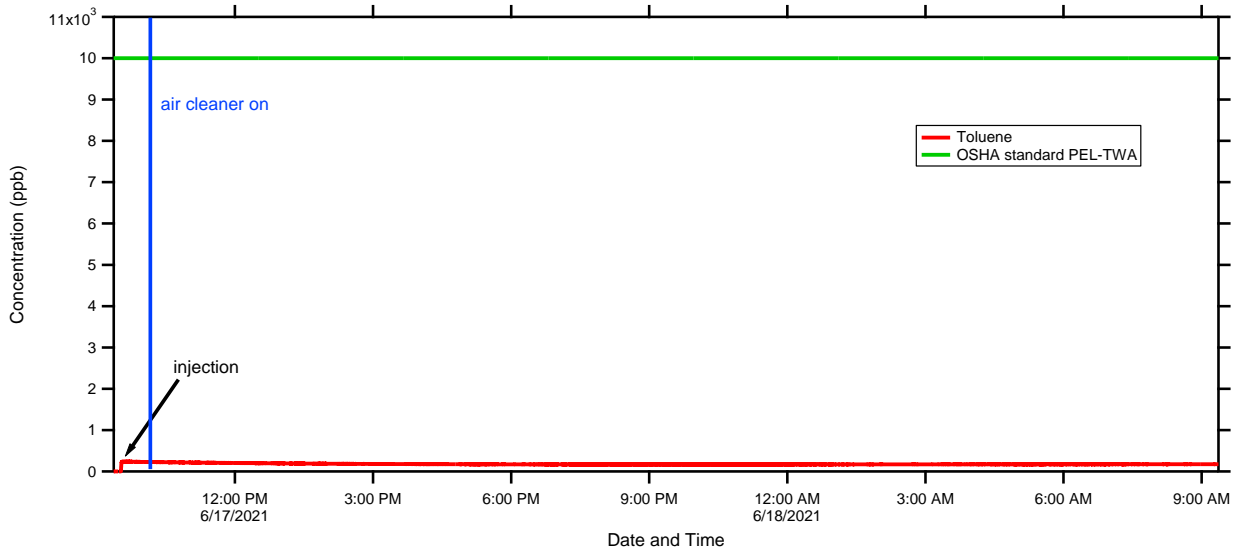


Figure 5. Toluene timeseries during 1st test and OSHA standard PEL-TWA.

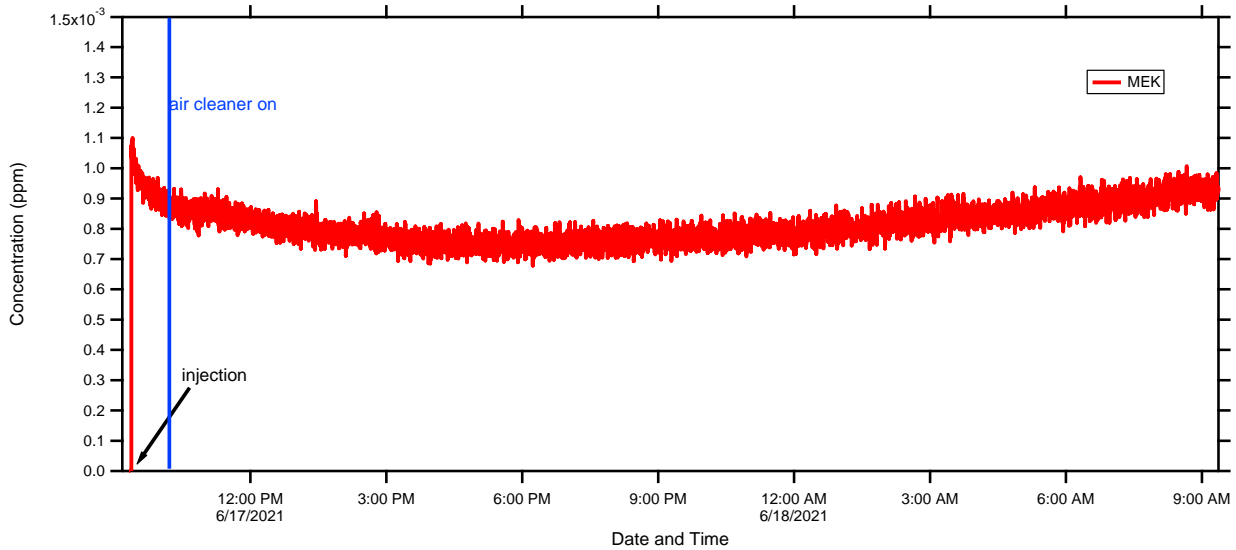


Figure 6. Methyl Ethyl Ketone (MEK) timeseries during 1st test.

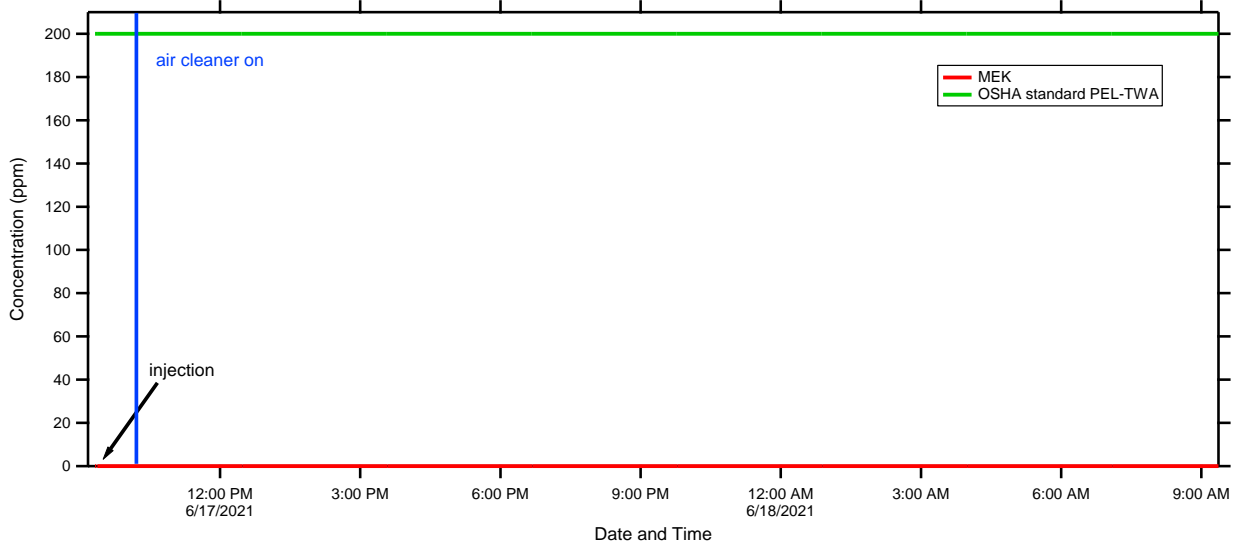


Figure 7. Methyl Ethyl Ketone timeseries during 1st test and OSHA standard PEL-TWA.

Should you have any questions or feel that we may be of further assistance, please do not hesitate to contact us.

The data was analyzed by

August 27, 2021

Air quality engineer/PTR-MS Scientist, Aikaterini Liangou

Date

The report was prepared by:

August 27, 2021

PTR-MS Specialist/Scientist III, Dr. Antonios Tasoglou

Date