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OZONE MITIGATION TESTS

AT THE APS

by

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OZONE MITIGATION TESTS AT THE APS

Abstract

Ozone is generated in the APS experimental stations whenever the x-ray beam has a chance to interact with air. Ozone concentrations in an experimental station have to be below a certain defined limit (current OSHA regulations specify 0.08 ppm as the maximum limit) before an experimenter can reenter the hutch. This limit is said to be currently under study for a downward adjustment. One method of depleting the ozone generated in an experimental station is mitigation through either adsorption or direct destruction. In recent tests, both methods were tried using commercially available units. Test results and some analytical predictions are presented.

Introduction

Ozone is generated in the APS experimental stations whenever the x-ray beam has a chance to interact with air. The lower energy photons disassociate the oxygen molecules which then attach to other oxygen molecules and form O_3 radicals. Ozone is harmful to electronic equipment (ISA 1985) and human beings [1]. The American Conference of Governmental Industrial Hygienists (ACGIH) set the present 8 hour threshold value (TLV) at 0.1 ppm with a short-term exposure limit (STEL) of 0.3 ppm. The National Ambient Air Quality Standards (NAAQS) for ozone is 120 parts per billion (ppb). Ozone concentrations in an experimental station have to be below a certain defined limit (current OSHA regulations specify 0.08 ppm as the maximum limit) before an experimenter can reenter the hutch. This limit is said to be currently under study for a downward adjustment.

The applicable OSHA standards are found in Title 29 of the Code of Federal Regulations, Part 1910, Subpart Z. The ozone permissible exposure limit (PEL) and method of compliance requirement have been in effect since May 29, 1971. The PEL was incorporated by reference (under Section 6(b) of Public Law 91-596, "The Occupational Safety and Health Act of 1970") from the 1969 ACGIH TLVs. These are not the only requirements that apply to ozone exposure at DOE facilities, nor do they address other fundamental questions (and requirements) concerning the management of ozone as would occur in some of the APS experiment enclosures [2].

One method of depleting ozone generated in an experimental station is mitigation through adsorption [3] or direct destruction. An O_3 adsorption unit through a series of activated charcoal filters was suggested (Purafil Model CA-500B). The direct destruction O_3 unit works on the principle of breaking down and converting ozone to oxygen through a catalytic converter. One such unit is by OREC Corporation, Model CDM -100, which

was used in the tests. The purpose of the test was to quantify the effectiveness of these two mitigation techniques as an alternate to direct suction and discharge.

Experimental Setup

The tests were conducted in ID-17 first optics enclosure (FOE) of the IMCA-CAT at the APS. The source is undulator A with the following relevant specifications.

Gap size [mm]	10.5
Ring Energy [GeV]	7.0
Ring current [mA]	100.0
Period length [cm]	3.3
Device length [m]	2.4
Number of periods	72.0
Max. magnetic field B_0 [T]	0.902
Characteristic energy E_c [keV]	29.4
Max. deflection parameter, K	2.78
Total power [kW]	6.0
Peak power [kW/mrad ²]	169.1

Figure 1 is a schematic of the experimental setup. Ozone is generated in a PVC "tee" as shown in Fig. 1. The 17-ID front end is terminated with the standard commissioning window assembly. This assembly consists of a 250 micron HOPG graphite filter, one 170 micron CVD diamond filter, and two 250 micron Be windows. In addition, there exists a separate 170 micron CVD diamond filter downstream of the Be window that covers the last Be window. A small amount of He flow was bled into the space between the last CVD diamond filter and the Be window to prevent oxidization of the window. The white beam traverses a short distance of air (about 10 cm) before it enters the tee. The tee is 4-in diameter PVC pipe and each arm of the tee is about 1 meter long.

Both ozone mitigation units have powerful fans to suck the room air through the tee. A precision vane anemometer was utilized to measure the induced air flow by the fans. In measurements, the Purafil unit was found to have 176 cfm (4.99 m³/min) and the OREC unit 109 cfm (3.09 m³/min) air flow into the tee. The flow was symmetric through both ends of the tee. With the OREC unit, the ozone tests were repeated by blocking the downstream end of the tee with a Kapton covered PVC pipe. In this case, the OREC unit would again induce 109 cfm air intake causing doubling the flow velocity in the PVC pipe.

The processed air through the units was freely dumped back into the room in a recirculation mode. In addition, however, a roof-mounted fan was allowed to pump 250 cfm (7.18 m³/min) experiment hall air into the room for the room ventilation. This setup creates air handling values typically found in experimental stations with ozone generation.

Measured quantities during the tests consisted of:

inlet ozone concentration	C_i (ppm)
exit ozone concentration	C_o (ppm)
inlet air temperature	T_i (C)
outlet air temperature	T_o (C)
room air temperature	$T_r = T_i$ (C)
flow rate	Q (cfm)

Inlet ozone concentration was measured at the top of the tee as shown in Fig. 1. Exit ozone concentrations were measured at the outlet from the ozone mitigation units (Fig. 1). Also, thermocouple points are indicated for various temperature measurements in Fig. 1.

The ozone concentration levels were measured using two IN-USA Inc., Ozone Analyzers (Series AFX, Model IN-2000) 0-10 and 0-100 ppm in full range, with a sensitivity of 100th of the scale. A hand-carried portable unit, Series AET, sensitive to 0.01 to 10 ppm level was used for the external ambient ozone measurements.

All tests were sequentially conducted in the 17-ID station at an 18 mm Undulator A gap at 100 mA ring current.

Results

The test data are presented in a series of plots in Figs. 2 through 10. These are as follows:

- Fig. 2 - Inlet ozone concentration with the Purafil unit operating
- Fig. 3 - Efficiency of the Purafil Unit in mitigating the ozone
- Fig. 4 - Inlet ozone concentration with the OREC unit operating
- Fig. 5 - Exit ozone concentration with the OREC unit operating
- Fig. 6 - Efficiency of the OREC Unit in mitigating the ozone
- Fig. 7 - Inlet ozone concentration with the OREC unit operating (with a Kapton covered pipe on the downstream side of the tee)
- Fig. 8 - Exit ozone concentration with the OREC unit operating (with a Kapton covered pipe on the downstream side of the tee)
- Fig. 9 - Efficiency of the OREC Unit in mitigating the ozone (with a Kapton covered pipe on the downstream side of the tee)
- Fig. 10 - Plot of the air temperature at the OREC unit inlet and outlet

Figure 2 shows that the inlet ozone concentration reaches a steady state level of about 15 ppm inside the tee. After mitigation via adsorbing over activated charcoal filter banks, this unit reduced the ozone levels to about 4 ppm level at the discharge, which is unacceptable.

Based on the above inlet and discharge ozone ppm levels, the Purafil filtration unit has a calculated 74 percent ozone mitigation efficiency at steady state (Fig. 3).

The OREC unit with the full tee has about 30 ppm ozone concentration generation at the inlet as seen in Fig. 4. At the discharge, the unit attains a steady state ozone level about 0.18 ppm as shown in Fig. 5. This corresponds to about 99.5 percent ozone removal level through the destruct catalyst (Fig. 6).

In the half-tee tests (the downstream leg of the tee is replaced by a Kapton-covered PVC pipe), the inlet ozone concentration rises to about 35 ppm (Fig. 7, at the same flow rate at 109 cfm but twice the air velocity in the tee). At the discharge, the steady state ozone levels are about .12-.13 ppm (Fig. 8). This corresponds to a removal efficiency >99.5 percent by the unit as plotted in Fig. 9.

One handicap of the ozone destruct unit using a catalytic converter is that it operates at a high catalytic bed temperature. OREC reported an operational temperature of 90.5°C (195°F) of the bed. At the exit, the steady state air temperature is supposed to be 52°C (125°F). Hence one has to be concerned about the rising experimental station temperatures in a recirculation mode. Fig. 10 shows the measured room and exit temperatures with the OREC unit under test conditions. The exit temperature gradually climbed to a quasi-steady level of 75-76°C with the room temperature at a steady 31°C as seen in Fig. 9.

In addition to the inside measurements, ambient ozone concentrations were also measured using the hand-held ozone analyzer at various locations around the experimental station. These measurements indicated the following ozone levels:

Station sliding door downstream: 0.05 to 0.09 ppm

Station sliding door upstream: 0.14 to 0.21 ppm

Station roof, downstream cable labyrinth opening (above the discharge point), 0.13 ppm

Station roof, middle cable labyrinth opening (above the tee), 0.23 ppm.

Station roof, upstream cable labyrinth opening (above the generation point), 0.27 ppm

In all cases, 3 to 4 feet away or above these measurement points, the ozone concentration levels fell rapidly to about the 0.04 - 0.05 ppm levels. True background was measured to be 0.0 ppm with the same unit.

Some conclusions from these tests will be presented below in the Discussion and Conclusions part.

Analytical Considerations

An attempt was made to predict the ozone generation rates under the test conditions. The analysis follows essentially the formulation and some of the measured quantities given in the reference by Weilandics et al. [4].

The ozone transport equation is given by the following generalized non-steady-state formulation:

$$dC/dT = GI/100n - \alpha C - \beta C - kIC \quad (1)$$

where

C, ozone concentration in	ppm	
G, ozone generation rate	mol/100 eV	
I, x-ray power density in generating ozone	eV/(cm s)	
α , chemical decay constant of ozone		(2)
$\beta = Q/V$ ozone removal rate (dilution)	1/s	
Q, the fan air flow rate through the experimental enclosure	m ³ /s	
V, volume of the experimental enclosure	m ³	
k, ozone destruction coefficient by the x-ray beam	cm ³ /V	
n	$2.462 \times 10^{13} \text{ mol}/(\text{cm}^3 \text{ ppm})$	

The non-steady and the steady state solutions to Eq. (1) are given in (3) and (4) respectively.

$$C(t) = C_{\text{sat}} (1 - e^{-\lambda t}) \quad (3)$$

$$C_{\text{sat}} = GI / (100 n \lambda) \quad (4)$$

where,

$$\lambda = \alpha + \beta + k I \quad (5)$$

Redefining,

$$I = P/V \quad (6)$$

where P is the total x-ray beam power expended to generate ozone in the experimental enclosure

A series of calculations were conducted to assess the value of P using the STAC-8 [5] code. This code is a FORTRAN program, developed at Spring-8 in Japan, that is used for shielding design calculations in synchrotron radiation applications in beamlines. It has been developed on the basis of the existing shielding design code, PHOTON, with added

features. These include: undulator source calculations, angular dependent coherent scattering cross sections, photon polarization effects, dose equivalent calculations, and build-up factors for shielding. The code generates synchrotron radiation source spectra, calculates photon attenuation through filters and windows estimating heat load in optical elements, and determines doses outside a shielding wall. Here the code was used to calculate the total x-ray power absorbed by the air in various path lengths (representing length of the experimental tee in our case). This power was assumed to be totally converted to ozone generation. Proper absorption of the various photon energies in the intervening media was accounted for as follows:

The white beam passes through a 250-micron-thick HOPG filter, one 170-micron-thick CVD diamond filter, two 250-micron-thick Be windows and another 170-micron-thick CVD diamond filter before it enters the experimental tee:

The photon flux from the undulator A beam after the filtering described above is given in Fig. 11 at different photon energy levels. For the purposes of this study, it suffices to say that, despite the substantial filtering as described above, the undulator A beam still retains a significant amount of photon flux in the 5 and 10 keV range to generate copious amount of ozone in air as the experiments bore out.

Figure 12 is a composite plot of P, power absorbed in air to generate ozone, for various air path lengths at 20, 50 and 100 mA beam currents and 11, 15 and 18 mm gap.

For the experimental conditions one should consider only the 200 and 100 cm long air paths lengths (full and half tee configurations respectively). However, it is generally agreed that ozone generation occurs mostly and vigorously in the upstream portion of a one meter long air path due to strong initial beam absorption; the later portions contributing rather minimally. Hence for the analytical calculations above, we considered only one-meter-long air path as the most representative case of the experiments.

Various constants and coefficients going into the above formulation in Eq. 1 were measured experimentally by Weilandics et al. or in their references. These values are listed below:

G, ozone generation rate, 2.69 mol/100 eV which is an integrated number for a given spectrum

α , chemical decay constant of ozone, $3.1 \times 10^{-4} \text{ s}^{-1}$

k, ozone destruction constant by beam, $1.4 \times 10^{-16} \text{ cm}^3 \text{ eV}^{-1}$

The value of " α " is in good agreement with the well-established 37 minute half life of the ozone decay. The situation is less certain with "G". It has been suggested to be as low as 1.46 mol/100eV by CERN researchers and as high as 6 to 13.8 mol/100eV in other studies. We used the value suggested by Weilandics et al.

The calculated value of the absorbed beam power in 100 cm of air path is given by 3.9 W/mrad-h/ mA. Considering that, at the commissioning window fixed mask, the beam width is about 0.18 mrad in the horizontal (4.5 mm at 25 m), an average value of 0.2 mrad is considered prior in the calculations. Hence the absorbed power at 100 mA beam current is $P = 78$ watts.

At the conversion rate of $1\text{ j} = 6.25 \times 10^{18}$ eV/s, 78 W corresponds to $P = 4.9 \times 10^{20}$ eV/s.

Then from Eq. (4), for an air flow rate of 109 cfm ($0.052\text{ m}^3/\text{s}$) in a pipe volume of 0.1 m^3 (1-m-long 10-cm-diameter pipe):

$$C_{\text{sat}} \approx 10\text{ ppm (at 100 mA beam current and 11 mm closed gap)}$$

This value is much below the measured ozone concentration levels in experiments at 100 mA and 18 mm gap.

Discussion and Conclusions:

The ozone generation and mitigation tests conducted at the APS in a white beam hutch using a powerful undulator beam show that, even after substantial filtration, there is potential for copious ozone generation, which needs to be mitigated. Of the several methods available for such mitigation, an adsorption technique drawing the ozone-laden room air through an activated charcoal-type filter unit and a direct destruction unit using a high temperature (195°F) catalytic bed were tested. Both units worked in a recirculation mode inside the station, which was further ventilated (air blowing in) by a 250 cfm blower.

Under identical experimental conditions, the generation concentration within a 2-m-long PVC tee was about 15 ppm for the charcoal unit and 30 to 35 ppm for the destruction unit. The flow rate within the tee was about 70 percent higher with the charcoal unit (176 cfm vs 106 cfm for the destruct unit). The charcoal unit, under the set conditions, could adsorb the incoming ozone only at a level in which the discharge concentration was at an unacceptable 4 ppm level.

The destruct unit performed rather well mitigating ozone down to 0.12 ppm under the experimental conditions. Oozing air from the station door clearances and the roof labyrinth measured from 0.05 to 0.27 ppm, which, within 3-4 feet, was reduced to the 0.05 ppm level. Of course, instead of blowing in (positive pressure), if the station ventilation air was sucked out (negative pressure), the oozing outside ozone levels would probably be negligible. Inside the station, the room temperature leveled at a constant 30°C with the hot working ozone destruct catalyst and the unit's powerful fan motor. This is about 6°C above the regulated temperature of the experimental station (an empty station devoid of any electronics or stand-by experimental gear). There are four objectionable aspects of the destruct units. The unit takes some space inside the tight

station; it is noisy; it is hot; and the destruct levels are above the expected 0.05 ppm levels. These are briefly discussed below.

The destruct unit is a mobile unit wheeled in and out easily on demand. It is simply plugged into a 220 V wall plug with an elephant trunk hose bringing the sucked ozone laden air into its intake pipe (4 in). It does require a space of about 2x3x5 (V) feet. However it can be left outside or operated on the station roof with antivibration pads.

As for the noise, the manufacturer offers quiet fans and sound muffling at additional cost as optional items.

As for the hot discharge, when used inside a station, the discharge air can be recirculated through a rather cheap chilled water air cooler.

As for the discharge ozone levels, which is the most important issue, the manufacturer claims that their present units are good to 99.98 percent mitigation and the older 100 cfm units that we have can deliver this kind of performance if the air flow is throttled down towards the 50 cfm level [6]. This needs to be further investigated.

The most desirable aspect of the destruct scheme is that it is mobile, available on demand, and can serve many stations without being affixed permanently in one location. Compared to permanently ducted-in schemes, it appears to have an economic advantage. The ozone control units used with it have an RS 232 interface for remote monitoring and alarms in addition to provision of the analog signals from multiple inputs.

The most important challenge is to resolve the applicable local or national regulations regarding direct discharge of the 0.05 to 0.07 ppm level O₃ into occupied spaces. This needs to be carefully reviewed.

As for the analytical predictions of the ozone generation rates with a white beam, while the formulation is properly posed, various coefficients required the formulation and/or the photon energy absorbed in air to create ozone need to be more rigorously determined in specific experiments. Otherwise, predicted ozone concentration counts calculated using the values found in meager literature on the subject are about two orders of magnitude lower than the experimental values.

Acknowledgments:

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References:

- [1] Lippman M., "Health effects of ozone: A critical review," J. Air Pollut. Control Association, 39: 672-695, 1989
- [2] Stockmeier Bruce, Oct. 1996, unpublished information, APS
- [3] Weschler Charles J. Shields, Helen C. and Naik V. Datta, "Ozone Removal efficiencies of activated carbon filters after more than three years of continuous service," OR-94-18-1, ASHRAE TRANSACTIONS 1994, V.100, Pt.2
- [4] Weilandics, Christopher, Rohrig, Norman, and Gmür, Nicholas F. "Ozone production due to synchrotron radiation," Nucl. Inst. Meth. Phys. Res., A266 (1988) 691-698
- [5] Arano Yoshihiro ed. Saramoto Nobuo, STAC8, Radi. Phys. Ed. Chem., 44, (1994 p. 133)
- [6] David Smith, Sept. 1996, private conversation, OREC

Figure Titles:

- Fig.1. Experimental setup in 17-ID first optical station
- Fig. 2 - Inlet ozone concentration with the Purafil unit operating
- Fig. 3 - Efficiency of the Purafil Unit in mitigating the ozone
- Fig. 4 - Inlet ozone concentration with the OREC unit operating
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- Fig. 7 - Inlet ozone concentration with the OREC unit operating (with a Kapton covered pipe on the downstream side of the tee)
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- Fig. 12 - Absorbed beam power to generate ozone for various air path lengths at 20, 50 and 100 mA beam current and 11, 15 and 18 mm undulator gap

OZONE MITIGATION EXPERIMENTAL SET-UP

FIG. 1

Ozone Generation and Destruction Levels

JTC
9/25/96

Ozone Destruct Unit Type : Purafil Model CA-500B

Unit Flowrate = 175 cfm

Configuration : Open Ozone Tee

Data taken in 17-ID-A on 9/23/96

FIG. 2

Ozone Destruction Efficiency

Ozone Destruct Unit Type : Purafil Model CA-500B

Unit Flowrate = 175 cfm

Configuration : Open Ozone Tee

Data taken in 17-ID-A on 9/23/96

FIG. 3

Ozone Generation and Destruction Levels

JTC
9/25/96

Ozone Destruct Unit Type : Osmonics Model CDM-100

Unit Flowrate = 109 cfm

Configuration : Open Ozone Tee

Data taken in 17-ID-A on 9/23/96

FIG. 4

Ozone Generation and Destruction Levels

Ozone Destruct Unit Type : Osmonics Model CDM-100
Unit Flowrate = 109 cfm

Configuration : Open Ozone Tee

Data taken in 17-ID-A on 9/23/96

FIG. 5

Ozone Destruction Unit Efficiency

JTC
9/25/96

Ozone Destruct Unit Type : Osmonics Model CDM-100

Unit Flowrate = 109 cfm

Configuration : Open Ozone Tee

Data taken in 17-ID-A on 9/23/96

FIG. 6

Ozone Generation and Destruction Levels

JTC
9/25/96

Ozone Destruct Unit Type : Osmonics Model CDM-100

Unit Flowrate = 109 cfm

Configuration : Ozone tee with downstream end sealed with Kapton

Data taken in 17-ID-A on 9/23/96

FIG. 7

Ozone Generation and Destruction Levels

JTC
9/25/96

Ozone Destruct Unit Type : Osmonics Model CDM-100

Unit Flowrate = 109 cfm

Configuration : Ozone tee with downstream end sealed with Kapton

Data taken in 17-ID-A on 9/23/96

FIG. 8

Ozone Destruction Efficiency

JTC
9/25/96

Ozone Destruct Unit Type : Osmonics Model CDM-100

Unit Flowrate = 109 cfm

Configuration : Ozone tee with downstream end sealed with Kapton

Data taken in 17-ID-A on 9/23/96

FIG. 9

Ozone Unit Discharge & Room Air Temperatures

JTC
9/25/96

Ozone Destruct Unit Type : Osmonics Model CDM-100

Unit Flowrate = 109 cfm

Data taken in 17-ID-A on 9/23/96

FIG. 10

Figure 11: Undulator A source spectrum (solid line) and the transmitted spectrum (dashed line) emerging out through the commissioning window assembly and an additional 175 micron CVD diamond filter.

Figure 12: Absorbed synchrotron beam power in various air path lengths with varying beam current and ID gap, as calculated by STAC8.