

PROTECTION OF WORKS OF ART FROM
DAMAGE DUE TO PHOTOCHEMICAL SMOG

Progress Report Through
September 1985

by

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1.0 INTRODUCTION

Experiments conducted in the early 1980's on a very small selection of modern artists' pigments showed that several pigments will fade dramatically if exposed to ozone at the levels found in Los Angeles photochemical smog. The objective of this research project is to provide a comprehensive assessment of the full scope of this fading hazard to works of art, and to determine the methods that can be used to protect works of art from damage due to photochemical oxidants. In order to achieve this objective, research is progressing on several fronts. Accomplishments to date will be summarized briefly, followed by several appendices that provide more detailed information on some aspects of the research.

2.0 THE FADING OF COLORANTS WHEN EXPOSED TO OZONE

Long-term ozone exposure experiments have been completed that involve a very large number of traditional organic artists' pigments. More than 150 dry powder pigment samples obtained from the Fogg Museum at Harvard and elsewhere were applied on paper and then exposed to 0.397 ± 0.007 ppm O_3 in the absence of light for twelve weeks at 72°F and 50% RH. The ozone concentration used is at the upper end of that actually found in the Los Angeles atmosphere during a heavy smog episode. The total ozone dose delivered to the pigments (concentration times duration) is equal to about 3 years of exposure to outdoor air in Los Angeles or to about 6 years

inside a typical air conditioned building. Results of these experiments are summarized in Table I, with colorants classified into several groups based on the color difference (ΔE) observed before and after O_3 exposure: Very Reactive ($\Delta E > 10$ after 90 days), Reactive ($\Delta E = 3 - 10$), Possibly Reactive ($\Delta E = 1 - 3$ after 90 days and the progression over time shows a monotonic trend toward fading), and Unreactive ($\Delta E < 1$ and no monotonic trend). It can be concluded at this point that a large number of traditional organic artists' pigments, if applied without protective binders or coatings, will fade if exposed to an atmosphere containing ozone.

3.0 THE CHEMISTRY OF OZONE ATTACK ON COLORANTS

The reaction products and mechanisms of ozone attack on artists' pigments are being studied. The purpose of this work is to confirm that the damage seen is consistent with ozone being the causal agent, and to gain insight into how ozone damage might be predicted and prevented.

Colorants investigated to date include alizarin lakes, curcumin, indigo and a synthetic triphenylmethane lake, each representing a different type of chemical structure. These colorants and related model compounds have been applied on a variety of substrates (cellulose, silica gel, teflon), exposed to ozone (both high levels for short times and low O_3 levels for 3 months), then extracted, concentrated and analyzed by direct probe injection into a mass spectrometer, or by gas chromatography/mass spectrometry. The major products of the ozone-curcumin reaction are tentatively identified as vanillic acid and isovanillin, products consistent with ozone attack on the olefinic bonds in the curcumin

TABLE I

Ozone Sensitivity of some Traditional Natural Colorants

<u>Very Reactive:</u>	Madder Lakes Indigo Dragon's Blood Curcumin Saffron Orpiment Realgar
<u>Reactive:</u>	Bitumen (Asphaltum) Carmine (Cochineal Lake) Indian Lake (Lac Lake) Gamboge Yellow Lake I Persian Berries Lake Weld
<u>Possibly Reactive:</u>	Indian Yellow Quercitron Lake Litmus Yellow Lake II (a different, possibly synthetic, one)
<u>Unreactive:</u>	Van Dyke Brown Sepia All other inorganics

molecule. Phthalic acid (or phthalic anhydride) has been found to be the major product of the gas phase/solid phase reaction of ozone with the calcium-aluminum lake of alizarin. By comparison, mass spectra indicate that reagent anthraquinone and alizarin dye when applied on cellulose or teflon do not react with ozone at all. The implication is that the very high ozone sensitivity of the alizarin lakes may be due to the creation of the lake and not to the reactivity of the anthraquinone ring system per se.

4.0 INDOOR POLLUTANT EXPOSURE IN SOUTHERN CALIFORNIA MUSEUMS

Whether or not ozone poses a hazard to works of art depends in part on whether or not ozone present outdoors is transferred to the indoor atmosphere of museums. A program of indoor/outdoor ozone measurements at eleven galleries and museums in Southern California (including the Getty) recently has been completed from which useful generalizations can be drawn about the ozone level expected as a function of building design. Buildings with rapid air exchange with the outdoors, no internal air recirculation, hard interior surfaces, no ozone removal equipment, and a high volume to surface area ratio show indoor O_3 levels 70% to 80% as high as those outside. Peak one-hour average ozone levels inside one such museum in Los Angeles (the Southwest Museum) have been observed at 143 ppb compared to 173 ppb outside, or 83% of the outdoor level. This is consistent with the performance observed in the gallery at the Sainsbury Center for Visual Arts in England where indoor ozone levels of up to 40 ppb were observed inside a modern art gallery in the presence of peak outdoor levels of 58 ppb (Davies et al., 1984). Southern California galleries with conventional air conditioning systems, a high internal air recirculation rate but no ozone

removal equipment show indoor ozone levels about 30% to 40% as high as those outdoors. Buildings without air conditioning that have little ventilation often show low O_3 levels, 10% to 20% of those outdoors, again due to O_3 depletion by reaction with building surfaces. It is now clear that ozone levels inside some Southern California museums are quite high, while others are quite low, and a systematic basis has been established for estimating the conditions inside buildings that have not yet been tested.

Ozone is not the only photochemically generated pollutant with the potential to damage materials. Los Angeles air also contains considerable quantities of oxides of nitrogen-derived air pollutants. Indoor/outdoor relationships for NO and NO_2 recently have been measured as part of this project at the newly constructed Virginia Steele Scott Gallery at the Huntington Library in San Marino, California. Pollutant removal systems at that site are confined to particle filtration only. Over the period October 30 - November 9, 1984, indoor NO averaged 37 ppb compared to 36 ppb outdoors, while indoor NO_2 averaged 38 ppb compared to 44 ppb outdoors. This survey suggests that in the absence of pollutant removal systems, indoor NO and NO_2 levels will be close to those outdoors.

5.0 MEASURES FOR THE PROTECTION OF WORKS OF ART FROM DAMAGE DUE TO PHOTOCHEMICAL SMOG

5.1 Pollutant Removal

Activated carbon air filtration systems are used for ozone removal by many major libraries and museums in the Los Angeles area. Facilities so equipped include the Huntington Library, Huntington Library Art Gallery, Los Angeles County Museum, Norton Simon Museum, J. Paul Getty Museum, and

Southwest Museum Library. Indoor/outdoor ozone measurements made at the Huntington Library Art Gallery in mid-summer of 1984 show peak indoor O_3 levels of 10 ppb in response to peak outdoor O_3 levels of 170 ppb, or about 94% removal. Pollutant removal systems at the Los Angeles County Museum of Art likewise were found to have removed over 90% of the ozone in air brought into the building. Conditions inside the Getty Museum galleries in Malibu depend on location within the building. In the second floor gallery tested (Room 203), the maximum ozone concentration in the activated carbon-filtered air stood at 9 ppb compared to an outdoor peak O_3 level of 95 ppb on that day, indicating greater than 90% O_3 removal. However, in a first floor gallery (Room 117) which is affected by cross-ventilation of outdoor air through open doors in the building, indoor O_3 reached 28 ppb in response to an outdoor peak of 75 ppb on the day tested, or 37% of the outdoor level. A peak one-hour outdoor O_3 level in Malibu of 133 ppb was noted on one of the 5 days studied, indicating that Malibu does experience O_3 levels above the National Ambient Air Quality standard for ozone (120 ppb in outdoor air based on human health criteria). For purposes of comparison, the draft ANSI standard for indoor air in rare book archives and libraries suggests that indoor ozone levels should be maintained below 1 ppb, based on conservation considerations.

5.2 The Effect Of Display Cases

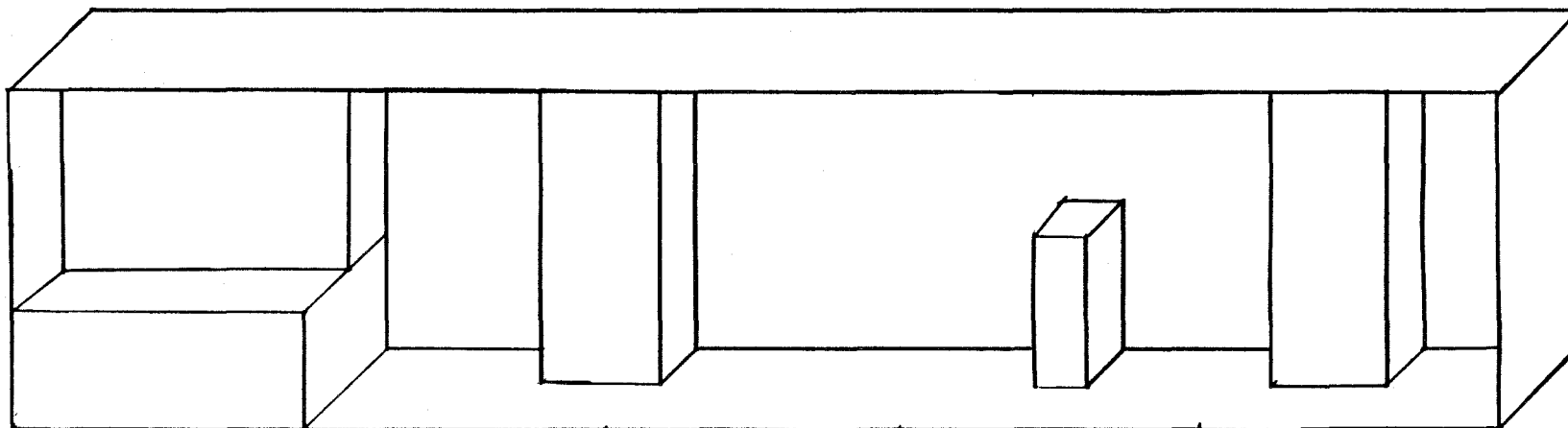
Although activated carbon air filtration has been demonstrated to be an effective means for ozone removal, the expense of installation may preclude its use in museums with low capital improvement budgets. Therefore, the effect of low-cost protection measures is being investigated. These measures include use of display cases and frames, or

protection of the pigments by application of binders or coatings.

Unusually high indoor O_3 levels were noted at the Southwest Museum. Therefore, that museum was chosen as the site for testing the effect of display cases as a barrier between works of art and the indoor air. A new procedure for determining the air exchange rate between the room and a loosely fitted display case was developed, based on injection of SF_6 (an inert tracer gas measurable in ultra-small quantities) into the display case. An illustration of these test results is given in the attached figures. That display case was found to have a characteristic time for air exchange with the room of 80 minutes. Ozone levels inside this display case were found to be about 10% or less of that found in the room air at the same time. This indicates that even loosely fitting display cases can be built that will afford considerable protection from ozone damage.

5.3 Development of a Mathematical Model for Prediction of Indoor Air Pollutant Levels

A computer-based mathematical model has been developed for predicting the indoor concentration of chemically reactive air pollutants. This calculation procedure can be used by architects and engineers to predict the indoor level of pollutants in buildings in advance of their construction, to diagnose the source of problems in existing buildings, and to test the likely effect of pollutant removal systems in advance of their installation. The model simulates the introduction of polluted urban air into a building's ventilation system. More than 15 chemical species are tracked including O_3 , NO , NO_2 , HNO_3 , formaldehyde, and higher aldehydes. Once inside, chemical reactions are followed between pollutants present in outdoor air and those emitted indoors (e.g., reactions between ozone from



Volume : 5.75 m
Surface Area (w/o objects) : 35.17 m
Surface Area of Gaps : .02 m

Five framed glass insets

2.76 cm <--> 1 m

Figure 1. Display Case 3

Decline in Tracer
Concentration

$$\ln \frac{[\text{SF}_6]}{[\text{SF}_6]_0}$$

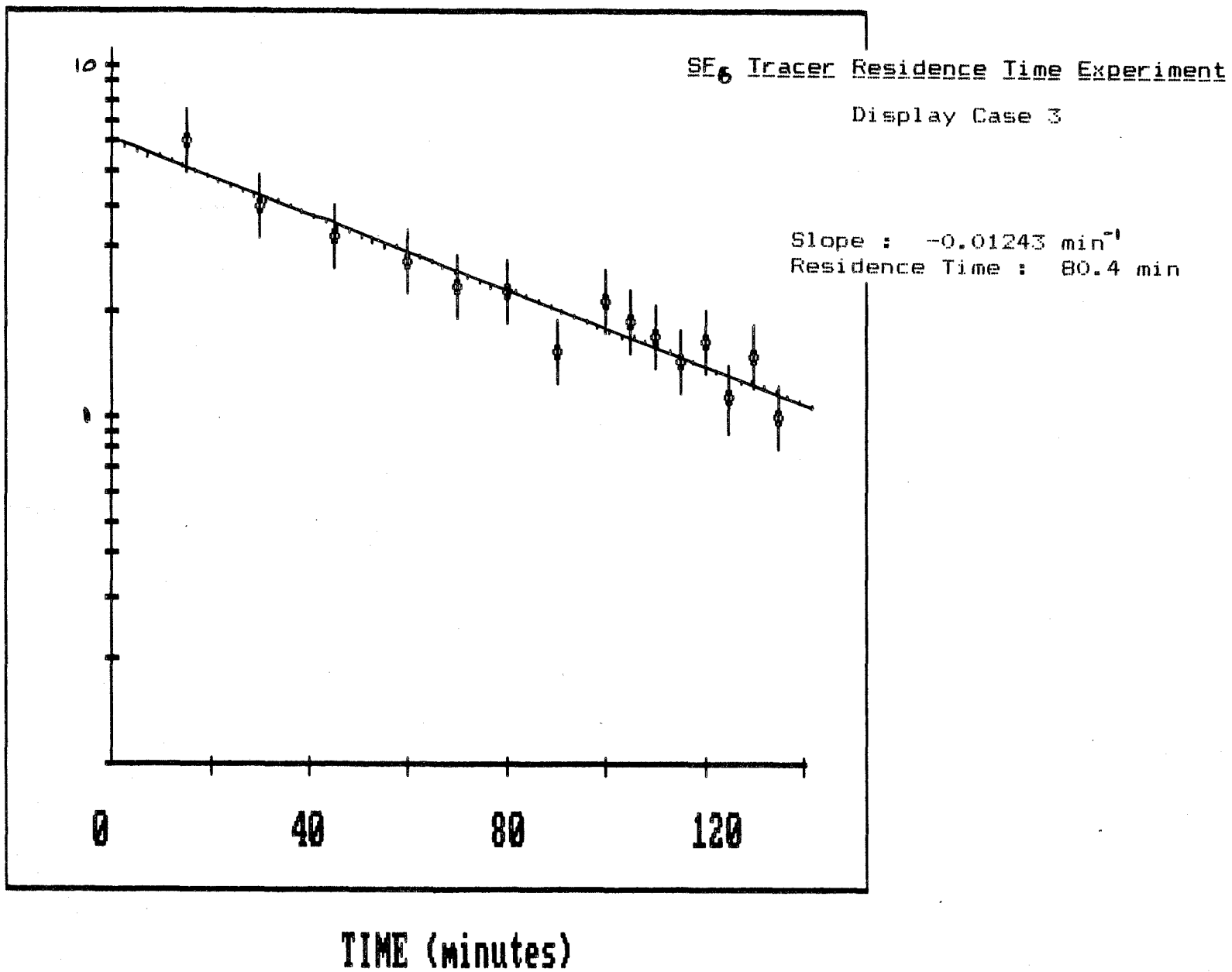


Figure 2.

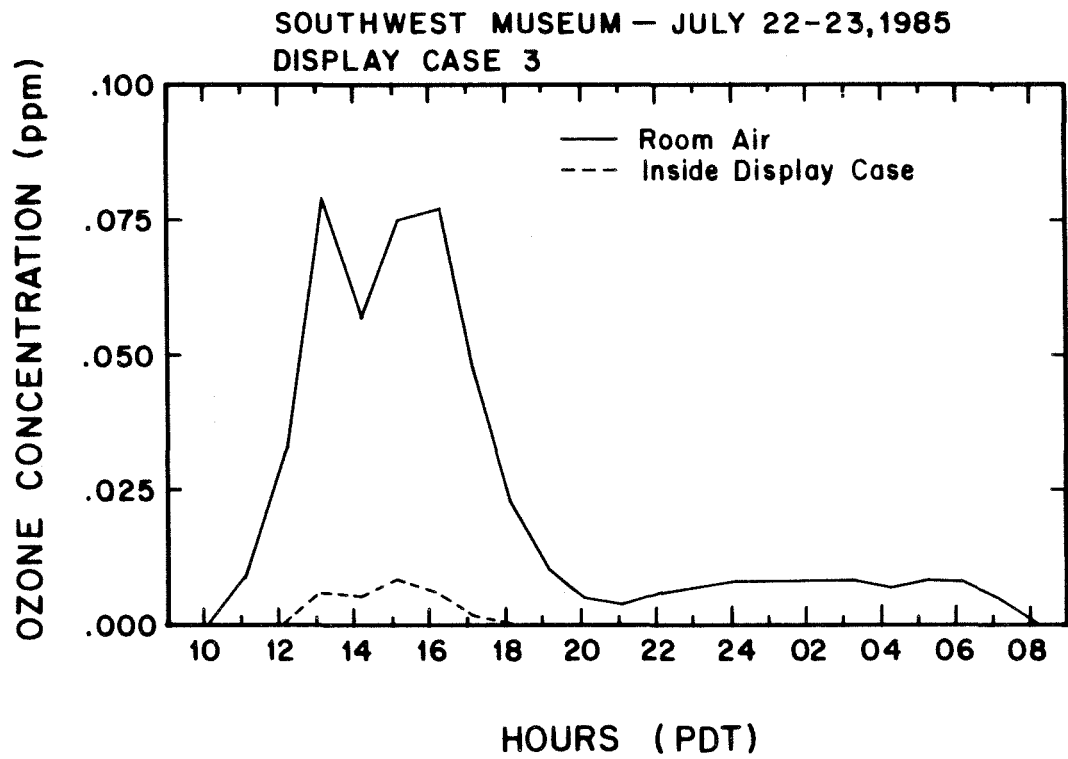


Figure 3.

outdoors and NO_x emitted from possible cafeteria stove top cooking operations). The flux of pollutants to building surfaces is computed, along with the effect of air recirculation through pollutant removal devices (e.g., activated carbon beds). The model has been tested using ventilation system data and data from our experiments conducted at the Scott Gallery on the Huntington Library grounds. Results for O_3 and NO_2 are shown in the attached figures.

6.0 COMMUNICATION OF RESEARCH RESULTS

During the past year, a manuscript entitled "Fading of Artists' Pigments due to Atmospheric Ozone" was accepted for publication in the 1985 edition of Wiener Berichte Uber Naturwissenschaft in Der Kunst. This work documents a series of experiments conducted during the year prior to receiving financial support from the J. Paul Getty Conservation Institute, but it is mentioned here because time available under the present grant made completion of this manuscript possible. At the request of Professor Norbert Baer of NYU, this paper also was presented orally before the session on protection of cultural properties at the 1984 annual meeting of the Air Pollution Control Association.

For the past year, Glen Cass has served on a panel of the National Academy of Sciences that is charged with recommending procedures for the protection of the collections at the National Archives. An understanding of indoor air pollutant levels in libraries and museums, and quantification of the effect of control devices on indoor pollutant levels, is necessary for the work of the National Academy committee. Data from the indoor/outdoor survey of pollutant levels in Southern California museums

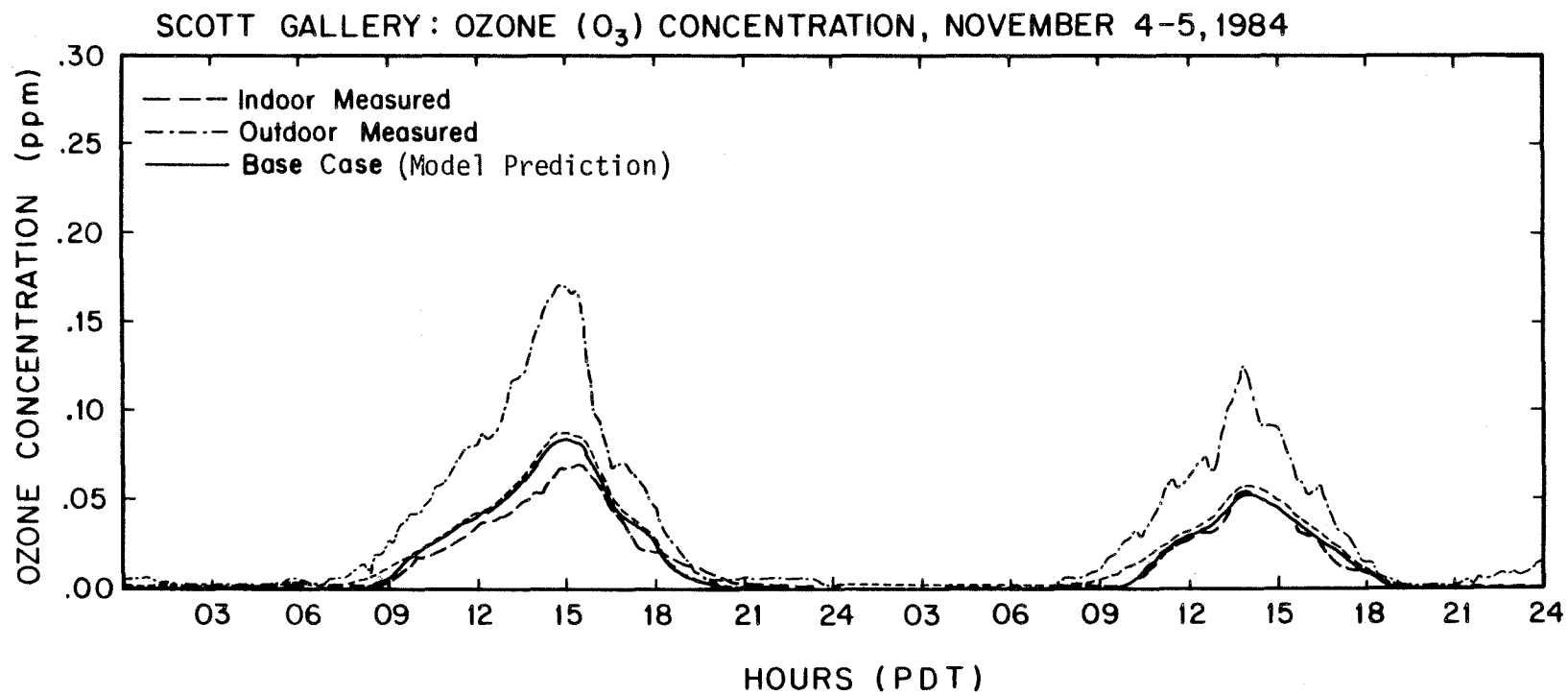


Figure 4.

SCOTT GALLERY: NO₂* CONCENTRATION, NOVEMBER 4-5, 1984

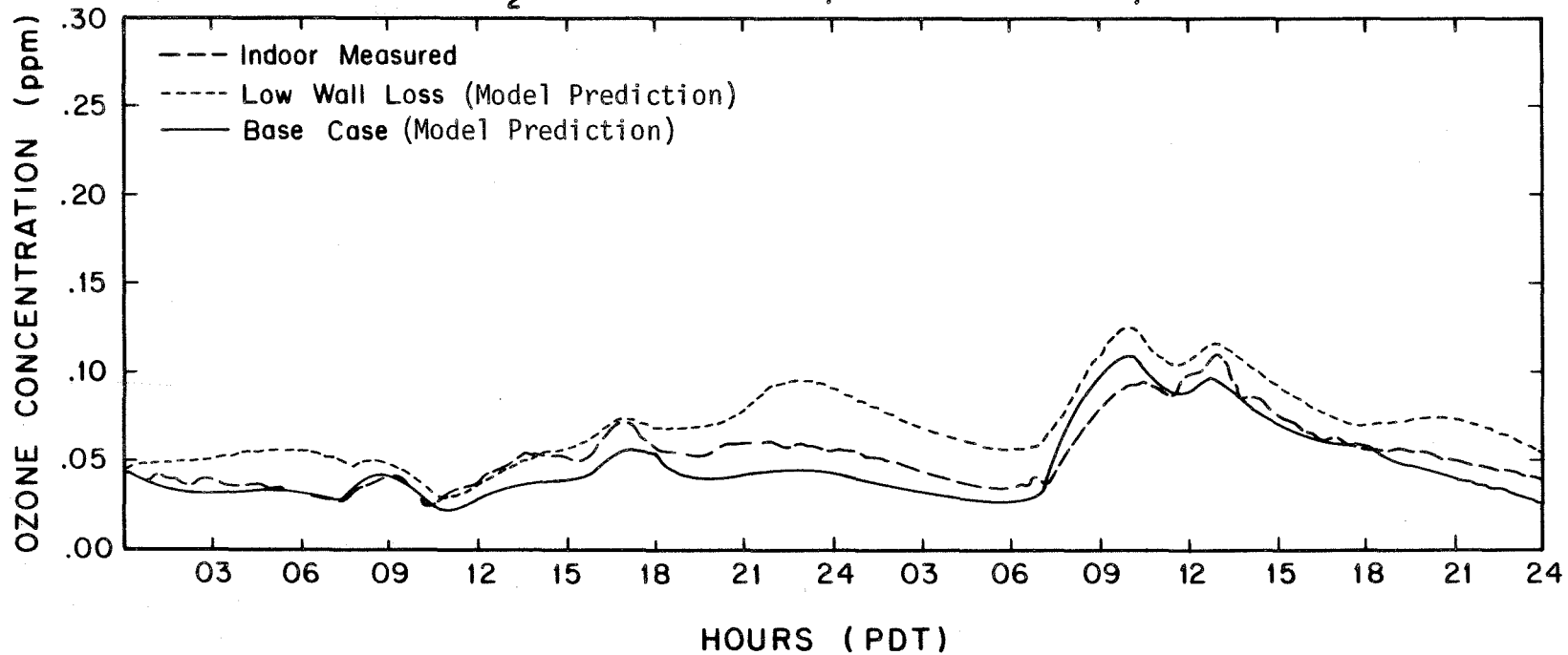


Figure 5.

and libraries conducted as part of the present Getty project are being used to help evaluate the pollutant removal system design effort at the National Archives.

Our present research project involved installation of new laboratory instrumentation, development of new sample preparation procedures, development of improved color measurement skills, followed by long-term ozone exposure experiments that by definition take a long-time to complete. As a result, we just reached the end point of several key experiments during September of 1985. Journal articles are in preparation at present covering (1) the survey of the ozone fading behavior of traditional artists' pigments, (2) the chemistry of ozone-pigment interaction, (3) indoor/outdoor relationships for ozone in Southern California museums, and (4) the mathematical modeling of chemically reacting systems in indoor air. Manuscripts (2), (3) and (4) above are in first-draft form at present. The long-term exposure experiment connected with manuscript (1) ended only about two weeks ago, and writing on that topic has just begun. We expect that these articles will be completed before the end of the present calendar year.

Appendix I

LONG DURATION OZONE EXPOSURE OF COLORANTS ON PAPER

A. OBJECTIVE

The overall objective of this series of experiments is to characterize the ozone fastness of traditional natural organic artists' pigments. To achieve that objective, screening tests have been run on over 150 pigment samples obtained from museum pigment collections. Particular attention is paid to the reaction of ozone with alizarin and madder lakes. Key questions in this case include:

- Are madder lakes inherently more ozone resistant than synthetic alizarin lakes (as has been observed for modern Winsor and Newton madder and alizarin lakes)?
- Does alizarin crimson fade "on shade," or are yellow intermediate decomposition products formed (as has been claimed in lightfastness studies)?
- How is the ozone fading affected by changes in relative humidity?

Finally, an understanding of the kinetics of the ozone fading of traditional artists pigments is sought.

B. EXPERIMENTAL

Pigments tested were obtained from pigment collections at the Fogg Museum, Balboa Museum, and Los Angeles County Museum of Art. In addition, several pigments of modern manufacture were included for study. Because the identity of pigments available in museum collections is reportedly unreliable, efforts are being made to verify the identities of the

pigments. The transmission spectra of solutions of the organic pigments have been taken, and the reported identities have been confirmed for most of the natural organic pigments, including all of the alizarin and madder lakes. The purchase of solution cells and manufacture of holders for these cells have made possible the recording of these spectra using the Match Scan in its transmission mode. This work is continuing, and soon will be extended to using thin layer chromatography for further characterization of organic lakes, and XRF and XRD for identification of inorganics.

A technique has been developed which allows preparation and study of very small (milligram) quantities of pigment on paper in the absence of any binder. A method for preparing very small samples is made necessary by the rarity of some of the pigments tested. A suspension of pigment in a volatile solvent was air-brushed onto a 1" x 2" piece of Arches hot-pressed 140 lb watercolor paper through a stainless steel mask with a 1 cm hole. This produced a 1 cm diameter spot in the center of the paper, and the pigment particles were embedded into the paper fibers so securely that routine handling of the samples does not dislodge them. An effort was made to produce samples whose reflectance at the wavelength of maximum absorption was about 40%, for it has been found that in this region the color change is most sensitive to changes in colorant concentration.

Reflectance measurements were made on the Match Scan using the small-area-view option to limit the sample size to approximately a 7 mm spot. This procedure reduces the signal-to-noise ratio of a measurement, but a jig made to hold the paper samples in a reproducible position in front of the sample port permitted precision on the order of 1 unit in ΔE . The instrument was calibrated vs. the standard white tile, and the calibration and reflectance spectra were all recorded with the specular

beam excluded (this allows subsequent calculation of Munsell notation). Reflectance data were taken at 2 nm intervals from 380 nm to 700 nm and were stored on floppy disks. Chromaticity coordinates and color differences (using CIE 1976 $L^*a^*b^*$ formula) are reported for CIE Illuminant C.

The exposure chamber was essentially unchanged from previous experiments. However, a computer data acquisition system has been built which continuously monitors the ozone concentrations and stores the values on floppy disks. A rebuilt ozone generation system allows much better control of the ozone levels and permits faster start-up times for the exposures. This feature makes possible the frequent removal of samples for measurement during the exposure, thus allowing the kinetics of the ozone fading to be observed.

Samples of all the colorants on paper were prepared and mounted on anodized aluminum panels. These panels were hung in the exposure chamber (adjacent to the chamber walls, samples facing in) and exposed to $0.397 \pm .007$ ppm O_3 at $72^\circ F$ and 50% RH in the dark for 12 weeks. The samples were removed and reflectance spectra taken after 1, 2, 3, 4, 6, 8, and 12 weeks.

C. RESULTS

I. Ozone Sensitivity of Traditional Natural Pigments

The screening of the ozone reactivity of a large number of traditional natural pigments (both organic and inorganic) has added several colorants to the list of those which should be considered ozone fugitive. The fading behavior over the twelve week exposure prompts the separation of colorants into several classes. These have arbitrarily been chosen as Very

Reactive ($\Delta E > 10$ after 12 weeks), Reactive ($\Delta E = 3-8$ after 12 weeks), Possibly Reactive ($\Delta E = 1-3$ after 12 weeks, and this color change shows a monotonic trend), and Unreactive ($\Delta E < 1$ and does not show a monotonic trend).

The results of the ozonescreening test are summarized in Table 1. Pigments which were represented by more than one sample have been classified according to the (approximate) average reactivity. (These results are still conditional, awaiting identity confirmation of the yellow lakes, Indian yellow, litmus, sepia, and bitumen. The identity of the reactive arsenic sulfides, orpiment and realgar, also must be confirmed by XRD.)

Two points should be noted here. The first is that the ozone fastness of a colorant is not necessarily related to its lightfastness (e.g., carmine is much more fugitive to light than madder lakes, yet it is more ozone resistant than the madder lakes). This experiment also emphasizes the need to test colorants of several manufacturers before conclusions are drawn as to their ozone reactivity. Prominent examples are the modern Winsor and Newton rose madder and carmine, which show unusually high ozone resistance compared to all the other madder and cochineal lakes tested.

2. Ozone Reactivity of Alizarin and Madder Lakes

Samples consisted of 18 alizarin lakes (4 modern and 14 "traditional") and 13 madder lakes (1 modern and 12 "traditional"). Upon exposure to ozone, all of the alizarin lakes and eight of the traditional madder lakes showed extreme reactivity ($\Delta E = 6-17$ after 12 weeks). Of the remaining madder lakes, four (including the 1 modern one) showed only moderate reactivity ($\Delta E = 3-5$ after 12 weeks), and one, reportedly "Burnt Madder Lake," showed no measurable reaction after 12 weeks.

TABLE I

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<u>Reactive:</u>	Bitumen (Asphaltum) Carmine (Cochineal Lake) Indian Lake (Lac Lake) Gamboge Yellow Lake I Persian Berries Lake Weld
<u>Possibly Reactive:</u>	Indian Yellow Quercitron Lake Litmus Yellow Lake II (a different, possibly synthetic, one)
<u>Unreactive:</u>	Van Dyke Brown Sepia All other inorganics

Several experiments are planned to explore the possible causes for the lower reactivity of these five madder lakes. The unreactive "Burnt Madder Lake" has presumably already been oxidized more than a normal madder lake, and the FTIR spectrum of this pigment should confirm this. A more detailed characterization of the dye composition (by thin layer chromatography) and the laking metal (by XRF or atomic absorption) may also help to explain the relative ozone resistance of these pigments.

A chromaticity ladder, produced by making color measurements on samples of different depths of shade, is shown in Figure 1. The chromaticity coordinates of an unexposed sample of this same alizarin crimson pigment falls on this chromaticity ladder. However, exposure to ozone causes an apparent yellowing to occur, then fading continues (progression towards the plain paper coordinates) along a new curve. This slight apparent color shift could result from light scattering by ozone reaction products on the surface of the paper or on the pigment particles themselves. This phenomenon might also result from the selective removal of small pigment particles, by ozone reaction, leaving the pigment layer with a slightly higher average particle size.

A second exposure experiment (in a different apparatus) is underway to compare the ozone reactivity of alizarin crimson at very low and very high relative humidities. Since measurable color changes occur after only one week of exposure at 0.4 ppm, these exposures should be completed soon. Preliminary results for very low humidity (RH much less than 20%) exposure to 0.4 ppm O_3 indicate extreme reactivity of alizarin crimson, very similar to the 50% RH results presented here.

This short-term apparatus next will be used for some preliminary studies of alizarin crimson fading at lower ozone concentrations.

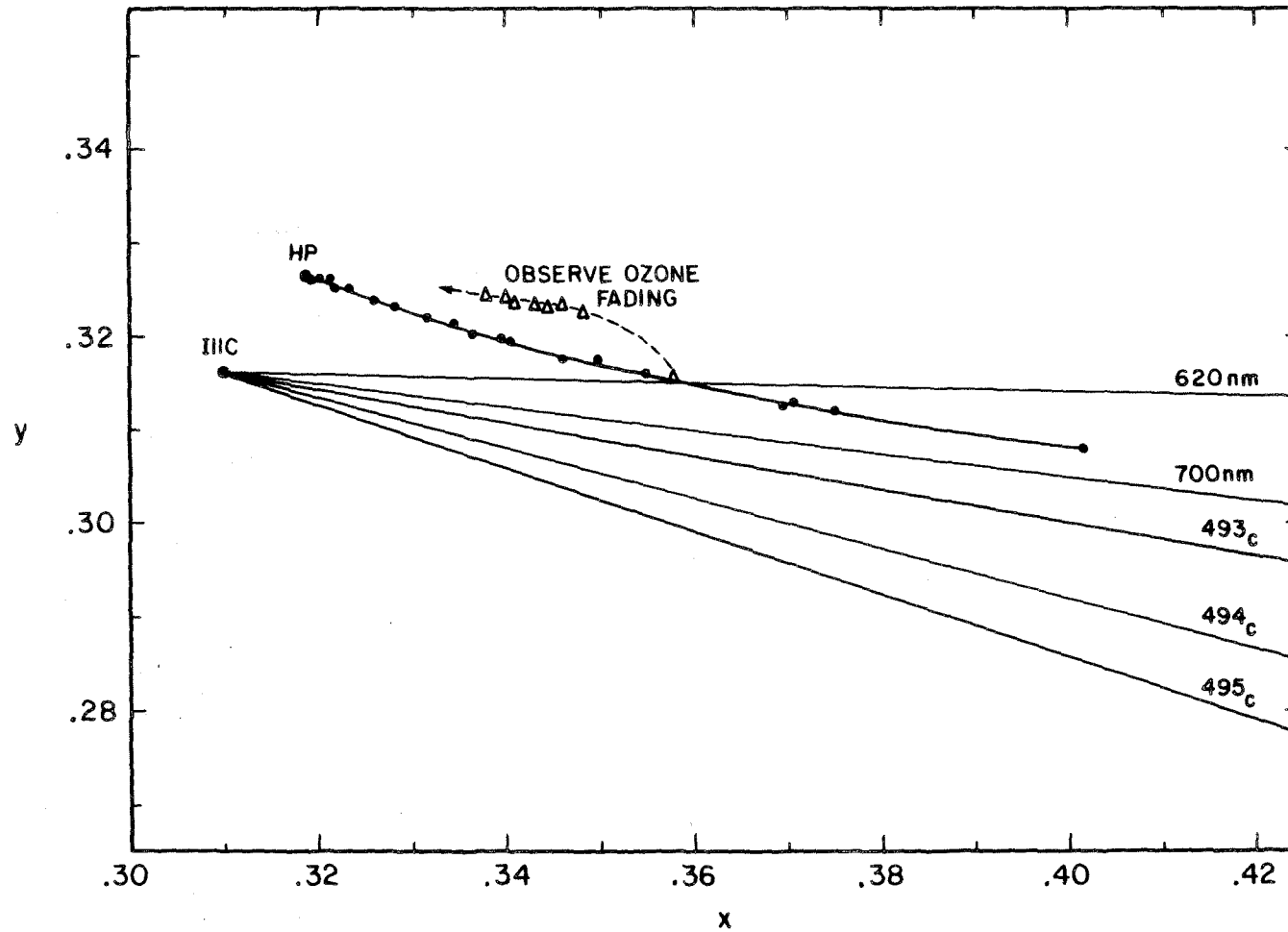


Figure 1. Chromaticity diagram illustrating the ozone fading of alizarin crimson on hot-pressed watercolor paper. The color of a sample is denoted by its chromaticity coordinates (x,y) , and the convergent lines index the apparent color of a sample (its "dominant wavelength") under CIE Illuminant C. The point labeled HP represents the color of the plain paper, and the solid dots and curve represent the colors of samples of alizarin crimson airbrushed onto paper at different densities. The triangles and dotted curve mark the color change observed as one sample of alizarin crimson is faded by exposure to 0.4 ppm ozone over a twelve-week period.

3. Kinetics of Ozone Fading

The ozone fading of colorants is expressed here in terms of ΔE (as calculated from the CIE 1976 $L^*a^*b^*$ equation) as a function of exposure time. For most of the colorants which fade upon ozone exposure, a plot of $\log(\Delta E)$ vs. $\log(\text{time})$ is linear over the duration of the experiment (or at least after the first week of exposure). The slope of this line proves to be very similar for many of the colorants, although the slopes for reagent indigo and saffron dyes appear consistently greater than the norm. In other words, the phenomenological relationship has been found:

$$\Delta E = At^n, \text{ where } n = .25 \text{ for a large number of reactive colorants.}$$

The slope of this curve may be greater at short times ($t < 1$ week) than at longer times ($t > 2$ weeks). This period of very large color change may be related to the observed yellowing which occurs in the short-duration ozone fading of alizarin crimson.

The dependence of ΔE on colorant concentration, particle size distribution, and the optical properties of the reaction products, is very complicated. It is unlikely, then, that these color measurements can be used to follow the depletion of colorant concentration, and thus to extract chemical kinetic rate information. However, the empirical observation of a simple, predictable ozone fading is very promising for the design of a simple colorimetric passive ozone monitor that might be used to gauge the integrated indoor O_3 levels over long time periods within museums.

4. Ozone Sensitivity of Oriental Colorants

A group of twelve oriental pigments obtained from the Fogg Museum and one dye (dayflower blue) obtained from Mrs. Keiko Keyes has been examined. Exposure to 0.4 ppm O_3 for 12 weeks caused severe fading of the indigo pigment and moderate fading of safflower and peony reds, dayflower

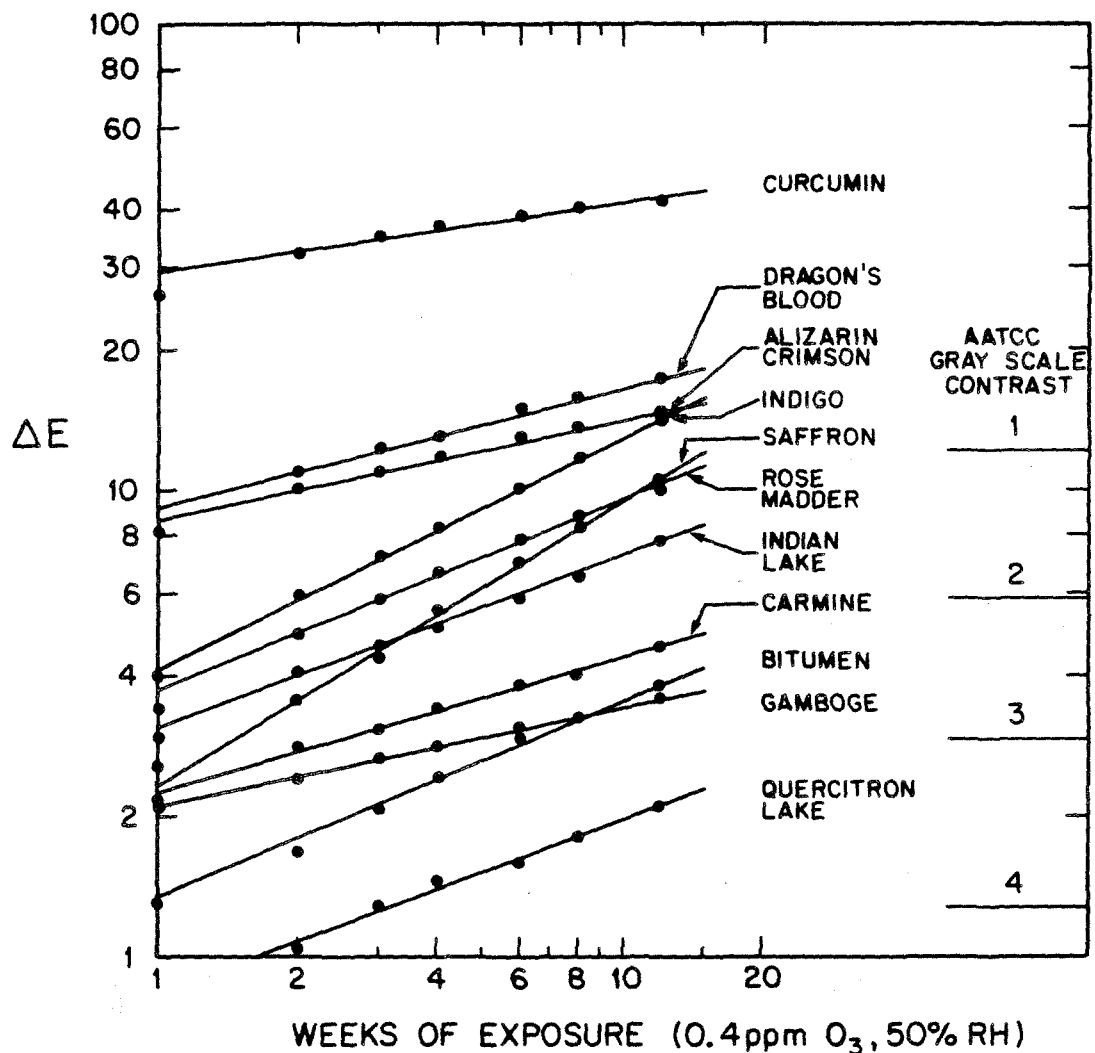


Figure 2. Logarithmic plot of measured color difference (ΔE) versus weeks of exposure to 0.4 ppm ozone for several traditional natural colorants. The color differences are calculated by comparing the color of the exposed sample to the color of the sample before exposure. Thus, the larger the value of ΔE (which is zero at zero exposure), the greater the extent of fading. Also shown are the ΔE values which correspond to steps on the AATCC Gray Scale, another standard measure of color fading.

blue, and a red lake (probably cochineal lake).

A much larger number of traditional Japanese colorants has been obtained very recently from Mr. Seiyu Yamazaki. These samples, in the form of dyed silk patches, represent the same dye/mordant/fiber combinations which were tested in Feller's study of the lightfastness of traditional Japanese colorants. A second ozone exposure experiment is planned and will include these silk cloths. The results of this study will provide a very interesting comparison of the relative ozone reactivity and lightfastness of these materials.

Appendix II

OZONE FADING OF ARTISTS PIGMENTS: REACTION PRODUCTS AND MECHANISMS

A. OBJECTIVE

The purpose of this series of experiments is to identify the reaction products of four of the colorants which have proven extremely sensitive to ozone exposure: alizarin crimson, curcumin, Basic Violet 14 lake (reportedly a major component of the Winsor and Newton "mauve" watercolor), and indigo. The product identification should verify that oxidation of the reactive chromophores by ozone is the cause of the observed color loss (rather than some secondary acid-base chemistry, for example). In addition, this study may provide some insight into the gas-solid reaction of ozone with colorants, a chemical interaction which has received very little attention.

B. EXPERIMENTAL

The samples of dyes and pigments used were all of modern manufacture. Alizarin crimson dry pigment and "mauve" tube watercolor were obtained from Winsor and Newton, and the indigo pigment was from Fezandie and Sperrle. Curcumin as well as reference and model compounds were obtained from chemical supply houses (Aldrich and Sigma).

Two different exposure experiments were employed in this study. In one experiment, colorants were applied by airbrush to silica gel or cellulose thin layer chromatography plates. These plates were then exposed to 0.4 ppm ozone at 70°F and 50% RH in the dark for 12 weeks. After exposure, the TLC support was extracted with methanol or methylene chloride to remove the

colorant and ozone reaction products. These liquid extracts were then concentrated by evaporation and analyzed.

In a separate apparatus, colorants were reacted as neat powders on Teflon membrane filters. These were exposed to high concentrations of ozone (approximately 10 ppm) at very low humidity for several days. After the ozone exposure, the powders were scraped from the filters and analyzed as solids.

Mass spectra were taken at the UCLA Chemistry Department facility. Three techniques were employed: 1) direct insertion probe with electron impact ionization (probe-EI); 2) direct insertion probe with chemical ionization using methane as reagent gas (probe-CI); and 3) gas chromatography/mass spectrometry with electron impact ionization (GC/EIMS). Mass spectra were used to verify the structures of the reactant compounds and to tentatively identify ozone reaction products. Product identities were confirmed by MS analyses of authentic samples of the suspected product compounds.

C. RESULTS

1. Curcumin

Mass spectra of unexposed curcumin on cellulose and Teflon confirm the structure of the reactant molecule is consistent with that of a pair of substituted aromatic rings joined by a seven-carbon chain which contains two olefinic bonds (at the 1 and 6 positions). Mass spectra of curcumin on silica gel show substantial decomposition of the dye even in the absence of ozone, so the results for this system will not be discussed here in the context of ozone degradation.

The major products of the ozone-curcumin reaction have been tentatively identified as vanillic acid and isovanillin (the corresponding aldehyde to vanillic acid). These products are consistent with electrophilic ozone attack at the olefinic carbon-carbon bonds, leading ultimately to cleavage of the carbon chain and substitution of carboxylic acid and aldehyde groups at the positions of the olefinic bonds. On the basis of other work on ozone-olefin and ozone-aromatic hydrocarbon systems, ozone attack at these olefinic sites of curcumin is expected to be much faster than reaction at the aromatic rings. Other minor products of the curcumin ozonation have been observed, and these may be secondary oxidation products of the major "first generation" products.

2. Indigo

This reaction system should represent an example of ozone attack on a highly substituted olefinic linkage. The indigotin molecule consists of a pair of fused ring systems which are connected by a double bond between a ring carbon of one system and a ring carbon on the other. Ozonation of this molecule in solution reportedly produces a ketone, formed by cleavage of this double bond and an oxygen atom insertion in place of the adjoining ring system.

Mass spectra of the indigo after reaction with ozone are forthcoming.

3. Alizarin Crimson

Alizarin crimson is the calcium-aluminum lake of the parent dye, alizarin (1,2-dihydroxyanthraquinone). This dye is a substituted polynuclear aromatic hydrocarbon, and thus offers only the possibility of ozone attack on these aromatic ring structures. Ozone reaction with aromatic hydrocarbons is in general relatively slow, much slower than ozone reactions with olefins. The rapid decolorization of alizarin lake seems

TENTATIVE MECHANISM FOR THE OZONE - CURCUMIN REACTION.

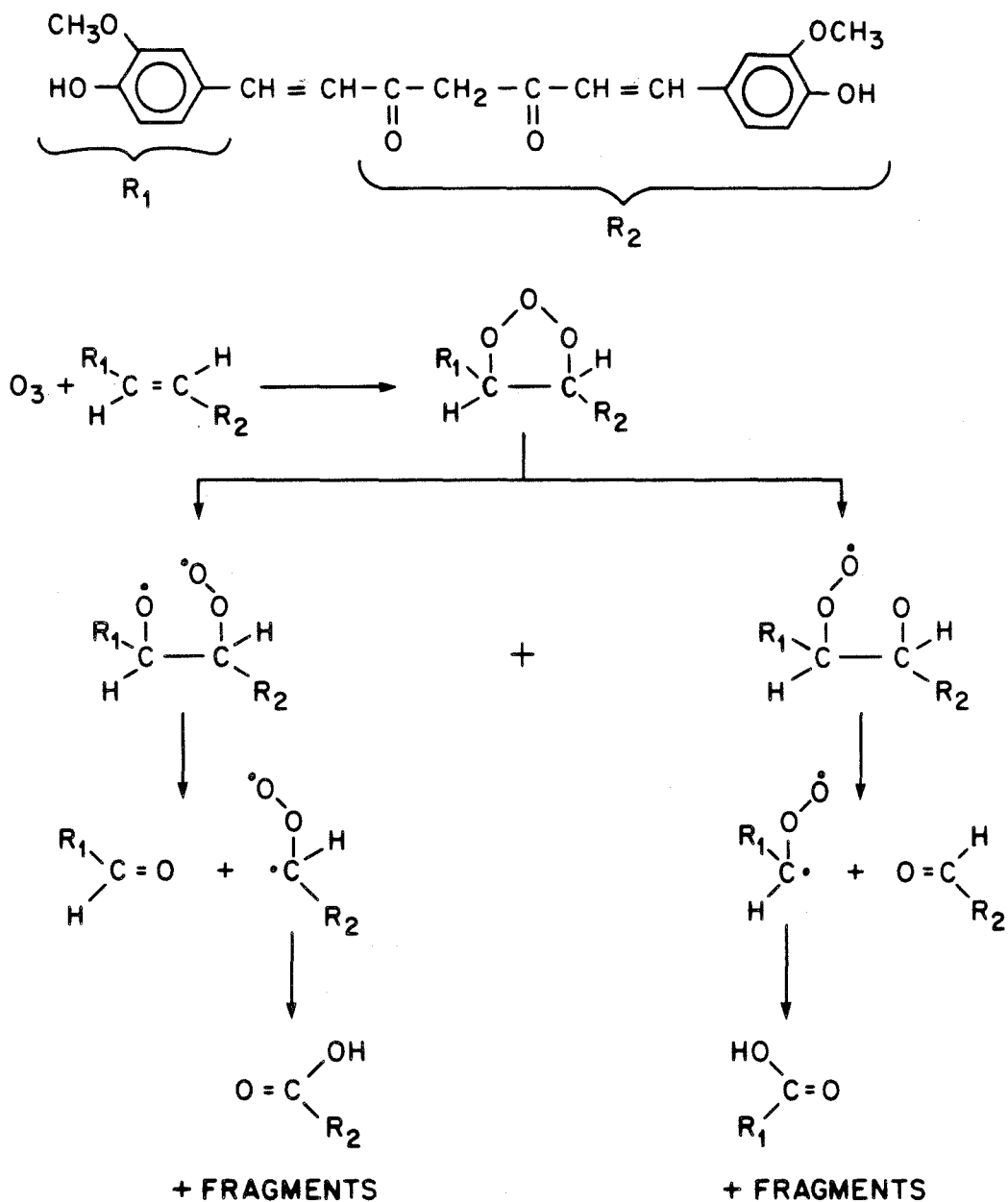


Figure 1

inconsistent with this trend, so an understanding of the details of this reaction may lead to a new insight into, and a better intuition about, the process of ozone fading.

By comparing the reaction of ozone with alizarin crimson, alizarin, and anthraquinone on the three different substrates (silica gel, cellulose, and Teflon), some trends emerge which may aid in elucidating a mechanism of ozone attack. Mass spectra indicate no reaction of anthraquinone with ozone on any of the three supports, a result consistent with the slow reaction of ozone with other aromatic hydrocarbons. Similarly, no reaction was observed with alizarin dye on Teflon and cellulose substrates. However, alizarin on silica gel showed extreme reactivity toward ozone, as did alizarin crimson on all three substrates. The major product in these reactive systems was identified as either phthalic acid or phthalic anhydride. These two compounds cannot be distinguished by mass spectrometry because of rapid water loss in the sample introduction. In addition, benzoic acid and a trihydroxyanthraquinone were minor products of the alizarin crimson ozonation, while other minor products of the alizarin on silica gel system have not been identified. Details of the mechanism by which ozone converts alizarin crimson to phthalic acid are under further investigation at present. The principal clue in this search is our finding that interaction with the laking metals or silica gel TLC plate surface is critical to transforming the slowly reacting alizarin dye into a rapidly degraded ozone-fugitive substance like alizarin crimson.

4. Triphenylmethane Lake

The observed color shift of Winsor and Newton's "mauve" watercolor upon ozone reaction is assumed to be due to the preferential reaction of the triphenylmethane lake component of this pigment blend. (The other

major component of this blend is reported to be copper phthalocyanine, which is relatively stable to ozone attack.) The structure of the parent triphenylmethane dye, Basic Violet 14, is reported to be three substituted benzene-type rings bound to a central carbon atom. One of these rings is attached via an olefinic linkage.

Once again, the mass spectrum of the lake pigment cannot be taken due to its low vapor pressure. Analysis of the reacted tube watercolor indicates that the major product of the ozonation is benzoic acid. The formation of benzoic acid is not consistent with the expected reaction sequence, which should produce substituted benzoic acids or benzoquinones as primary products. Further studies of ozone reaction with the parent dye, Basic Violet 14, are underway.

Appendix III

INDOOR/OUTDOOR RELATIONSHIPS FOR OZONE IN SOUTHERN CALIFORNIA MUSEUMS

1.0 INTRODUCTION

In order to adequately assess the effect of atmospheric ozone on works of art outside the laboratory, it is first necessary to determine the extent to which outdoor ozone is transferred to the inside of museums and art galleries. It is this indoor concentration of ozone to which important works of art are actually subjected.

2.0 EXPERIMENTAL PROGRAM

The first step in this program was a field study. Air quality measurements were made at a number of museums and art galleries. The following Southern California facilities were used as locations in the field study:

<u>Date</u>	<u>Site, Location</u>
7/3 to 7/5 1984	Pasadena Historical Museum, Pasadena
7/11 to 7/12 1984	Southwest Museum, Los Angeles
7/13 to 7/15 1984	Southwest Museum Library, Los Angeles
7/25 to 7/26 1984	Virginia Steele Scott Gallery at the Huntington Library, San Marino
7/27 to 7/29 1984	Huntington Art Gallery, San Marino
7/30 to 7/31 1984	Montgomery Gallery, Claremont
8/1 to 8/2 1984	Lang Gallery, Claremont
8/7 to 8/8 1984	Villa Montezuma, San Diego
8/9 to 8/10 1984	Serra Museum, San Diego
6/28 to 6/30 1985	Los Angeles County Museum of Art, Los Angeles
7/2 to 7/15 1985	J. Paul Getty Museum, Malibu

Simultaneous indoor and outdoor ozone concentrations were measured at each site using a matched pair of DASIBI UV photometric ozone monitors. The blueprints of each facility were examined to determine the volume, surface

area, and materials of construction used in each building. Each building's ventilation system was documented. A hot wire anemometer was used to measure air flow into and out of ventilation ducts, doors, and windows at each site. From this information, the air exchange rates and retention times for ozone destruction by reaction with building surfaces could be determined.

3.0 RESULTS

Each of these sites fell into one of three distinct groups: not air conditioned (Pasadena Historical, Southwest, Lang, Villa Montezuma, and Serra); air conditioned but without an activated carbon air filtration system (Scott and Montgomery); and air conditioned with activated carbon filters (Southwest Museum Library, Huntington Art Gallery, Los Angeles County Museum of Art, and J. Paul Getty Museum).

Buildings that operate without conventional air conditioning are arrayed in a distribution between two extremes: those with rapid infiltration of outdoor air and those with little air exchange with the outdoors. Rapid air exchange can be achieved, as at the Southwest Museum, if forced exhaust fans induce a once-through flow of outdoor air. At the other extreme, community galleries operating in converted private mansions with the doors and windows kept closed often experience very slow air exchange rates with the outdoors.

The Southwest Museum and the Serra Museum are examples of buildings with rapid air exchange but no air conditioning:

- (1) Southwest Museum -- A high-power fan in an open window forces about 5000 cubic feet of air per minute out of the building and

initiates convection throughout the main portion of the building. Two exhibit rooms are largely unaffected by this continuous flow. Many open windows and doors allow large amounts of circulatory air to pass through the building.

- (2) Serra Museum -- Open doors and windows, generally large in size and few in number, provide for ventilation at this facility. One open door facing the ocean is subjected to a steady breeze.

Ozone concentrations observed inside these buildings are generally quite high, on the order of 70 to 80% of the ozone level in the outdoor air that is brought into the building:

Site	Date	Outdoor Max. O ₃ (ppm)	Indoor Max. O ₃ (ppm)	Percentage of Outdoor O ₃
Southwest	7/11/84	0.090	0.132	69%
Southwest	7/12/84	0.143	0.173	84%
Serra	8/09/84	0.034	0.049	69%
Serra	8/10/84	0.022	0.028	79%

Conditions at the Southwest Museum are illustrated in Figure 1, attached.

In contrast, museums that lack air conditioning and that have very low air infiltration rates show some of the lowest indoor O₃ levels observed:

- (1) Pasadena Historical Museum -- A few open windows, mostly on the second floor, provide poor ventilation. An exception occurs when the site is used for luncheons or meetings, when the large front door is left open for the duration of the meeting. On normal days, the building is reasonably well sealed, and outdoor air enters the building at a very slow rate.

- (2) Lang Gallery -- One open window and one door open during public

SOUTHWEST MUSEUM - JULY 12, 1984

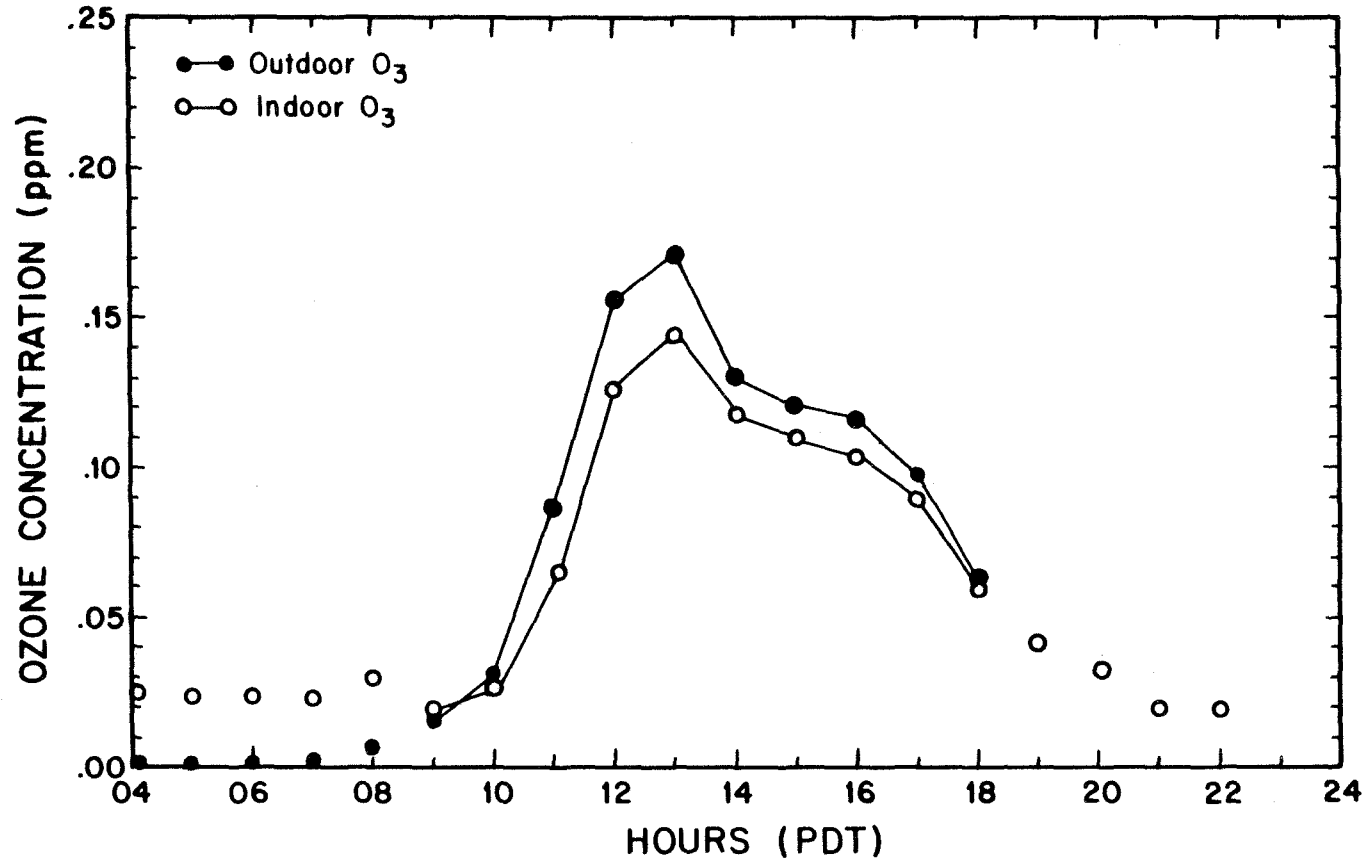


Figure 1

hours provide the ventilation at this site. The door is shut when the staff leaves for lunch or in the evening. Very little outside air is permitted to enter the facility. One or two fans circulate the air within the facility, but these fans do not force exchange with air outdoors.

Site	Date	Indoor Max. O ₃ (ppm)	Outdoor Max. O ₃ (ppm)	Indoor O ₃ as Percentage of Outdoor O ₃	Comment
Pasadena Historical Society Museum	7/3/84	0.098	0.166	59%	1
Pasadena Historical Society Museum	7/4/84	0.025	0.155	16%	2
Pasadena Historical Society Museum	7/5/84	0.019	0.133	14%	3
Lang	8/1/84	0.030	0.140	20%	4
Lang	8/2/84	0.017	0.168	10%	5

Comment Code:

- 1) Worst case. Luncheon held with front door open during peak ozone hours.
- 2) Building sealed for holiday.
- 3) Normal operations.
- 4) Front door open in morning and late afternoon; closed otherwise.
- 5) Building closed. This is the best case and is observed only when the building is sealed.

With the exception of the cases where the front doors were left wide open, indoor ozone levels in the above facilities are very low, on the order to 10% to 20% of the outdoor O₃ level.

Conditions at the Villa Montezuma represent an intermediate condition between the rapidly ventilated vs. stagnant non-air conditioned galleries. A dozen or so open windows and a door provide ventilation, while numerous

fans circulate the air within the facility. An up-draft can be felt in the stairwells of this largely vertical building as the warm interior air rises to be replaced at the ground level. Consequently, many of the first floor doors and windows serve as air inlets.

Site	Date	Indoor Max. O ₃ (ppm)	Outdoor Max O ₃ (ppm)	Indoor O ₃ as Percentage of Outdoor O ₃	Comment
V.Montezuma	8/7/84	0.014	0.042	33%	1
V.Montezuma	8/8/84	0.022	0.045	49%	2

Comment:

- 1) Normal operations.
- 2) More windows open than on previous day.

A summary of peak ozone concentrations observed inside museums with air conditioning but without activated carbon filtration follows:

Site	Date	Indoor Max. O ₃ (ppm)	Outdoor Max. O ₃ (ppm)	Percentage of Outdoor O ₃
Scott	7/25/84	0.043	0.179	24%
Scott	7/26/84	0.065	0.221	29%
Montgomery	7/30/84	0.060	0.150	40%
Montgomery	7/31/84	0.067	0.171	39%

Ozone levels in these buildings are reduced relative to the experience at the Southwest Museum because air is recirculated through the building many times, increasing the retention time for ozone loss by reaction with building surfaces. One possible reason why Montgomery Gallery experiences interior ozone levels that more closely approach those outside is that less of the air at this facility is recirculated more than once through the air

conditioning system than at the Scott Museum. This is supported by the shorter lag-time between the occurrence of outdoor and indoor O_3 peaks. Montgomery had an average lag-time of less than 20 minutes, while Scott's lag-time was close to 40 minutes. Based on the above data, we can expect that a museum with a typical air conditioning system will experience ozone levels inside the building that are 30 to 40% of that observed outside, with the peak concentration indoors lagging that outdoors by about one half hour.

Ozone concentrations within museums fitted with activated carbon air filtration units were generally quite low. Typical O_3 removal efficiencies greater than 90% were observed, and indoor O_3 levels were usually found to be below 0.01 ppm. A typical example of O_3 removal performance by the activated carbon system at the Huntington Art Gallery is attached as Figure 2. Exceptions to this rule were found in certain portions of the J. Paul Getty Museum in Malibu. A detailed report on the Getty facility is given in Appendix IV to this progress report.

HUNTINGTON ART GALLERY - JULY 28, 1984

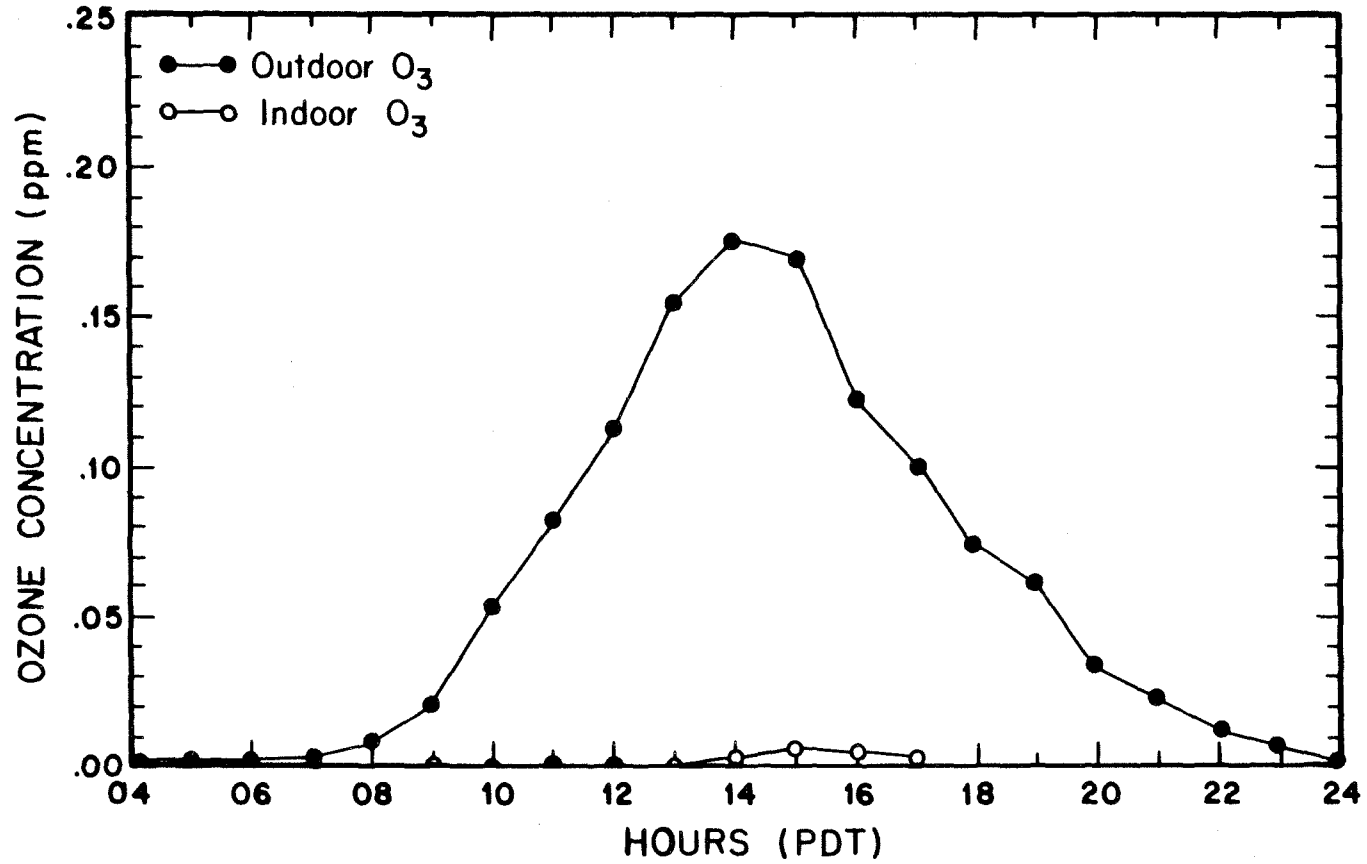


Figure 2

Appendix IV

INDOOR/OUTDOOR OZONE CONCENTRATION RELATIONSHIPS AT THE J. PAUL GETTY MUSEUM, MALIBU

1.0 SUMMARY

Indoor and outdoor ozone concentrations were monitored continuously for 24 hours for a total of five days at four different indoor sites at the J. Paul Getty Museum in Malibu. The indoor sites included 1) the administrative area, 2) the conservation laboratory, 3) gallery room 203, and 4) gallery room 117. The results show that Malibu can experience high outdoor ozone levels, similar to western Los Angeles. The second floor gallery that is served by a well-sealed air conditioning loop containing activated carbon filtration shows indoor ozone levels less than 10% of those outdoors. The first floor gallery that receives cross ventilation through open doors in the building shows peak indoor ozone levels 37% as high as those outdoors.

2.0 EXPERIMENTAL PROCEDURE

Indoor/outdoor ozone levels were monitored at four indoor sites at the J. Paul Getty Museum in Malibu. The first site was within the administrative area of the building in the first aid room on July 2, 1985. The conservation laboratory in the ranch house was monitored for two days, July 3 - 4. A paintings gallery on the second floor of the museum, Room 203, was monitored on July 8. Finally, a gallery on the first floor, Room 117, one room removed from the central courtyard, was monitored on July 15. In all cases, outdoor air quality was monitored at a location behind the

laboratory building next to the ranch house.

Ozone concentrations were continuously monitored using a pair of Dasibi ozone monitors, each drawing air at 2 liters/minute and accurate to within $\pm 3\%$. In preparation for a measurement period, the ozone monitor was located in a stable position at the desired site, within reach of a source of power and protected from direct sunlight. An air inlet line, including a filter for removal of airborne particulate matter, was connected making sure that the air inlet was sufficiently removed from the instrument's exhaust port. The monitor was allowed to warm up for 30 minutes, routine performance checks were made, and the strip chart recorder was readied. Ozone concentrations were continuously recorded for approximately 24 hours, or more.

Analysis of the data required conversion of the strip chart recordings to hourly average levels. This was accomplished by taking about 15 readings per hour and then averaging. There are three sources of uncertainty in the data. The ozone monitor itself is accurate to within $\pm 3\%$. Conversion of the recordings to hourly averages by hand is probably accurate to within ± 0.001 ppm. Possible drift of the strip chart recorder paper, although compensated for, introduces another ± 0.001 ppm variability.

3.0 RESULTS

Results of this series of experiments are illustrated in the attached graphs. Even though the Getty Museum is located quite far from the urban center where pollution sources are most concentrated, the outdoor levels of ozone on occasion were nearly as high as the levels in Los Angeles. During

the sampling days at the Getty, the outdoor daily peak concentration ranged from a low of 0.067 ppm on July 4 to a high of 0.133 ppm on July 3.

The air conditioning system serving the main building at the Getty Museum is equipped with activated carbon air filtration units. Activated carbon filters ordinarily would be expected to lower indoor ozone levels by at least 90% relative to the ozone levels in the outdoor air supplied to the air conditioning system inlet. Indoor ozone levels observed in second floor gallery room 203 reached a peak of only 0.009 ppm on July 8, indicating better than 90% removal of ozone relative to the outdoor peak of 0.095 ppm on that day. At other locations in the building, ozone removal efficiency was observed to be lower than expected. On July 15, when the outdoor ozone concentration peaked at 0.075 ppm, indoor concentrations reached 0.028 ppm in gallery Room 117, a first floor area one room removed from the central courtyard. This represents indoor ozone levels 37% as high as those outdoors. We suspect that unfiltered outdoor air is entering the first floor air conditioning loop via infiltration through open doors on the first floor level. Alternatively, the activated carbon beds may be ready for regeneration. In the administrative area of the building, on July 2 the peak ozone concentration was 0.027 ppm, 53.5% of the outdoor concentration at the same hour and 22.4% of the outdoor peak of 0.104 ppm. In the conservation laboratory on July 4, the peak was 0.021 ppm compared to an outdoor peak of 0.067 ppm. It is interesting to note that the ranch house conservation laboratory sometimes shows indoor ozone levels at night that are higher than those outdoors at night. This suggests that there may be a small indoor ozone source in that building due to continued operation of electrical equipment that is less well vented at night than during the daytime.

J. PAUL GETTY MUSEUM, MALIBU - JULY 8-9, 1985
GALLERY ROOM 203

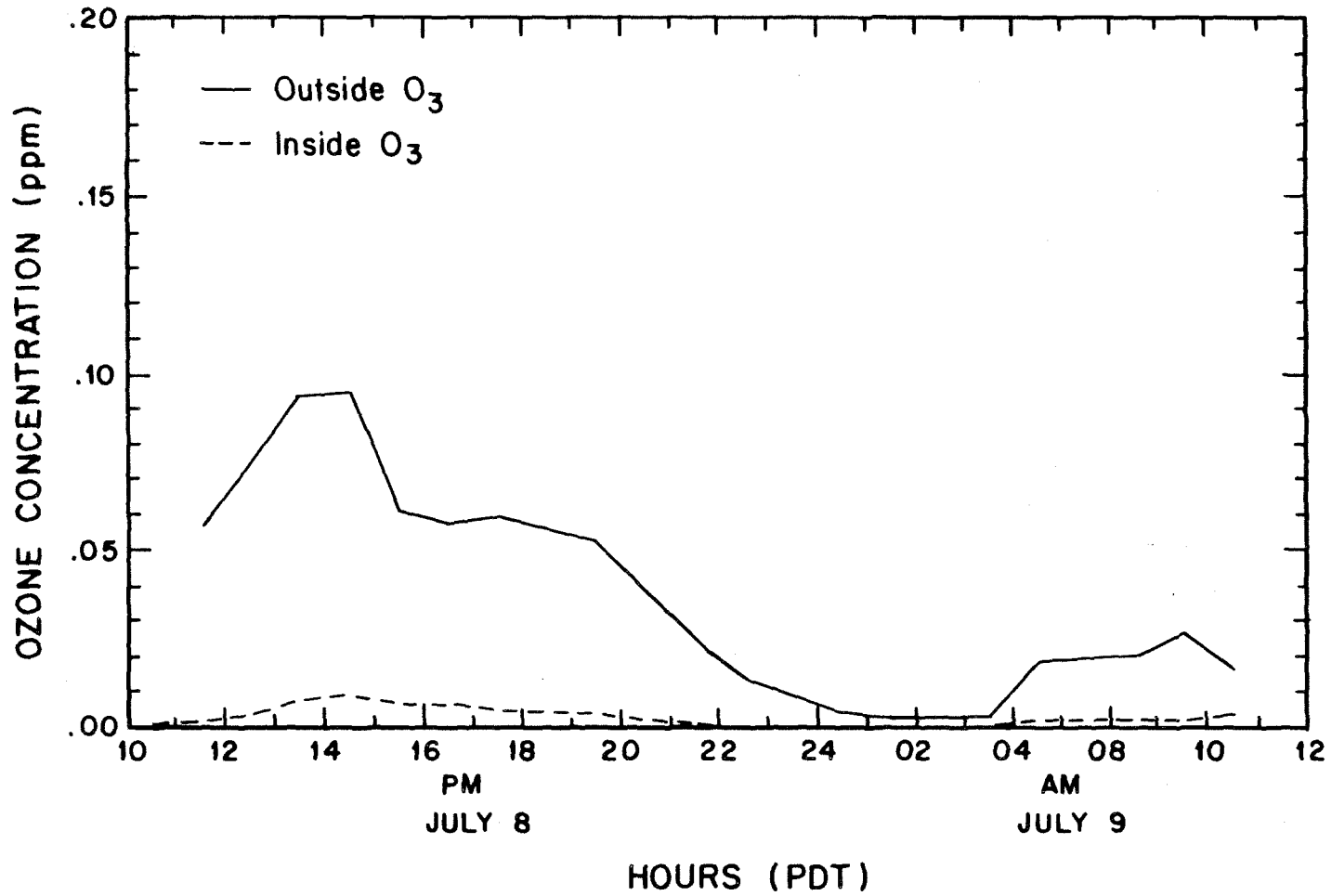


Figure 1

J. PAUL GETTY MUSEUM, MALIBU — JULY 15-16, 1985
GALLERY ROOM 117

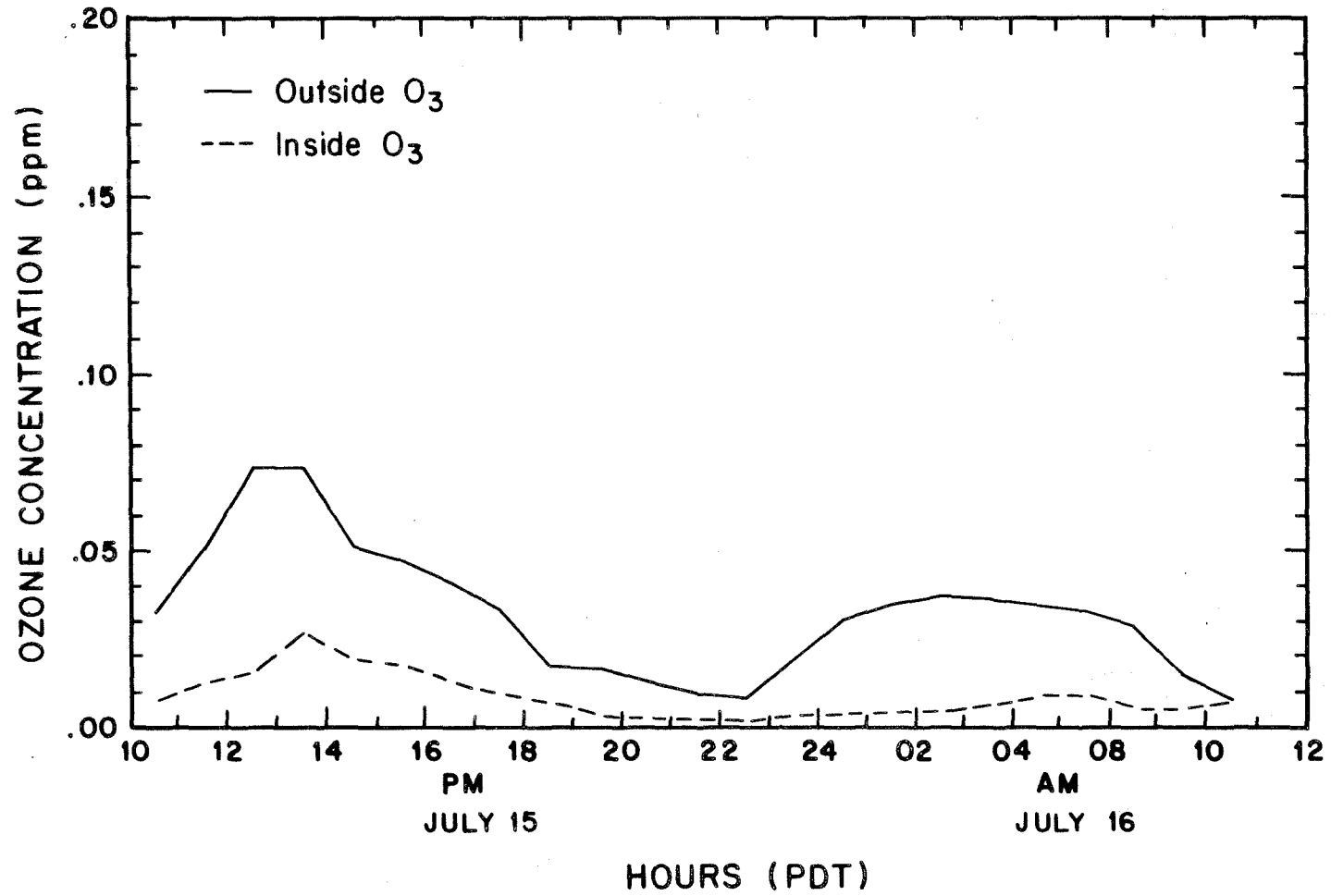


Figure 2

J. PAUL GETTY MUSEUM, MALIBU — JULY 2-3, 1985
ADMINISTRATIVE AREA

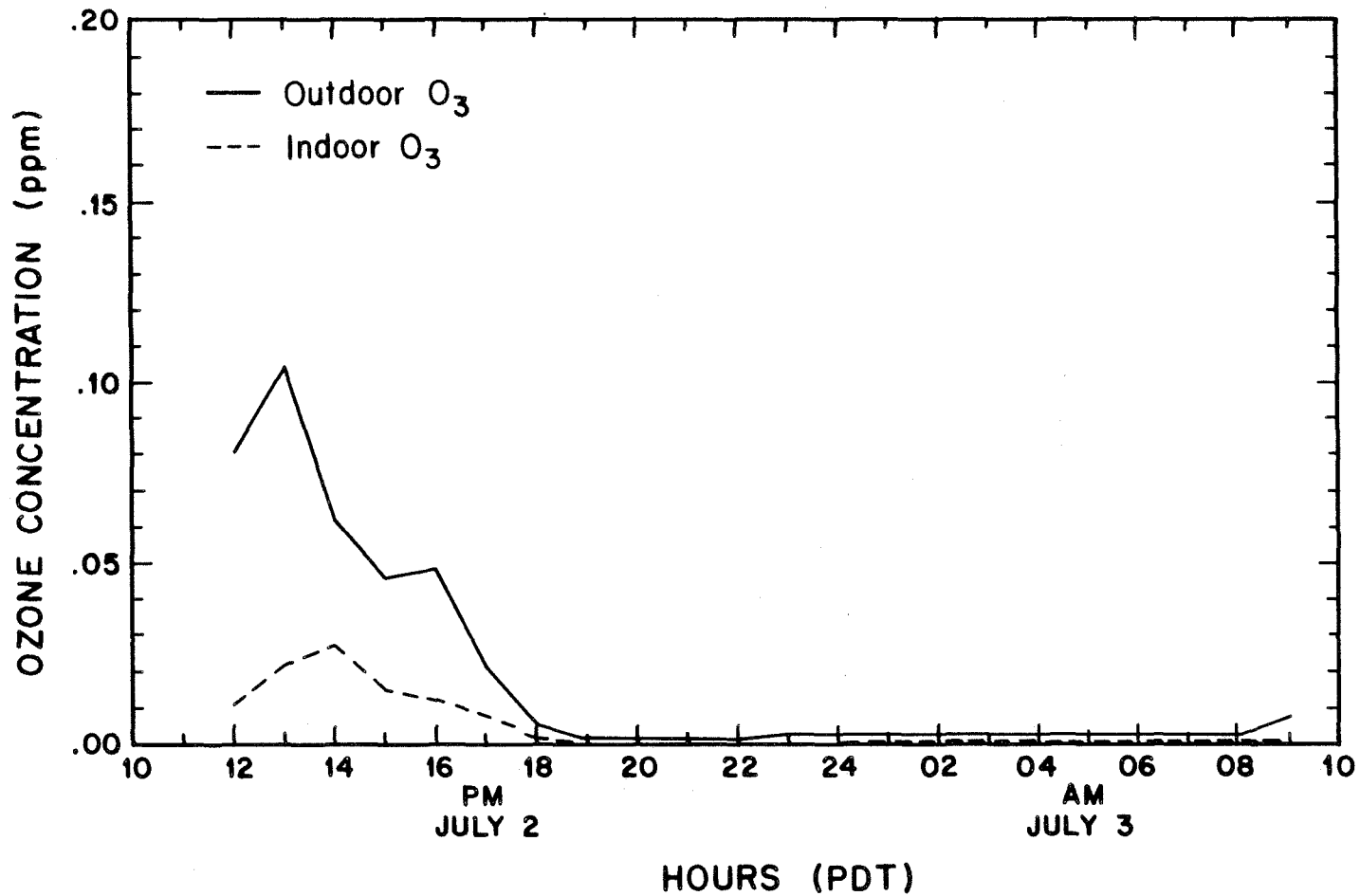


Figure 3

J. PAUL GETTY MUSEUM, MALIBU — JULY 3-4, 1985
RANCH HOUSE CONSERVATION LABORATORY

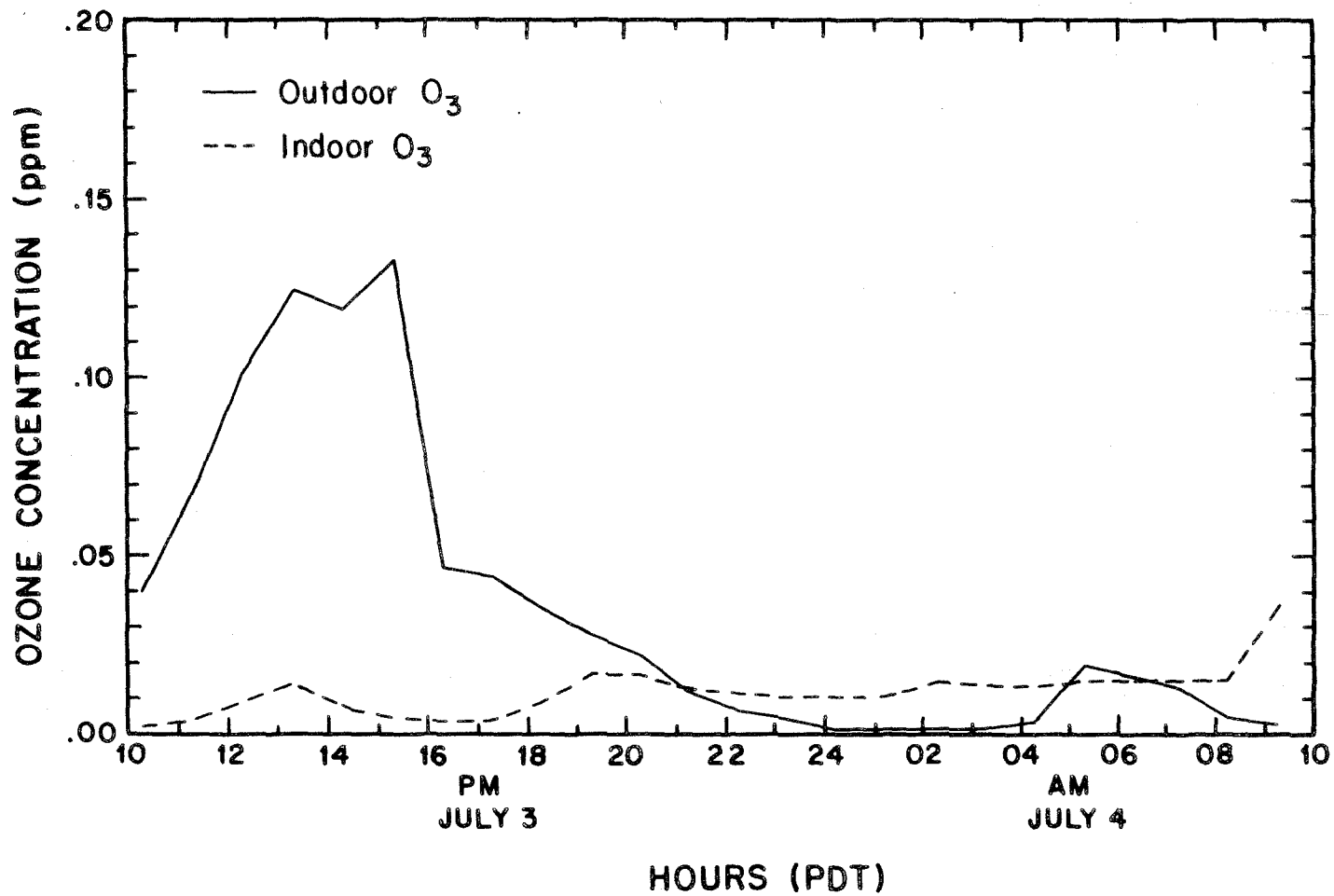


Figure 4

J. PAUL GETTY MUSEUM, MALIBU — JULY 4-5, 1985
RANCH HOUSE CONSERVATION LABORATORY

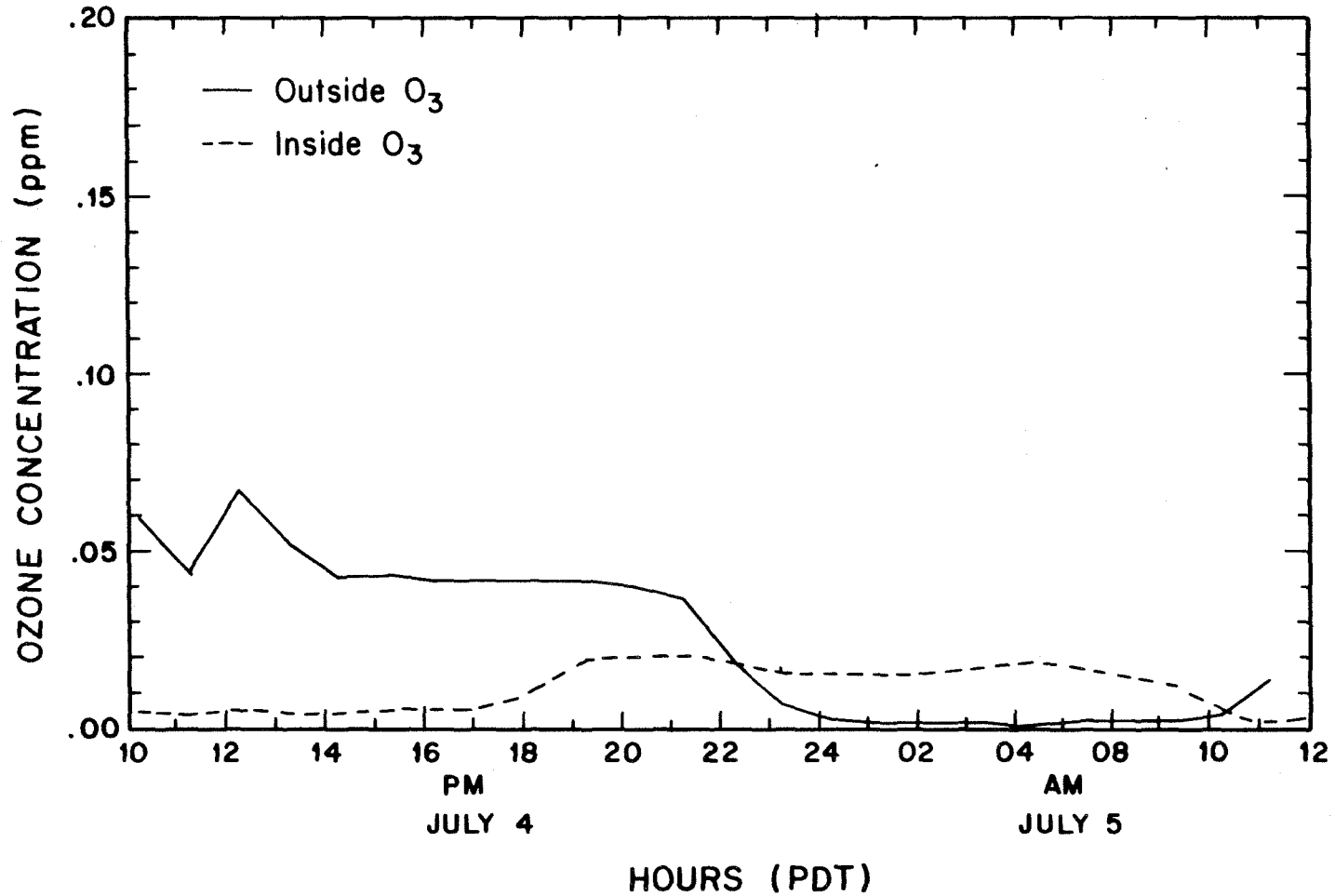


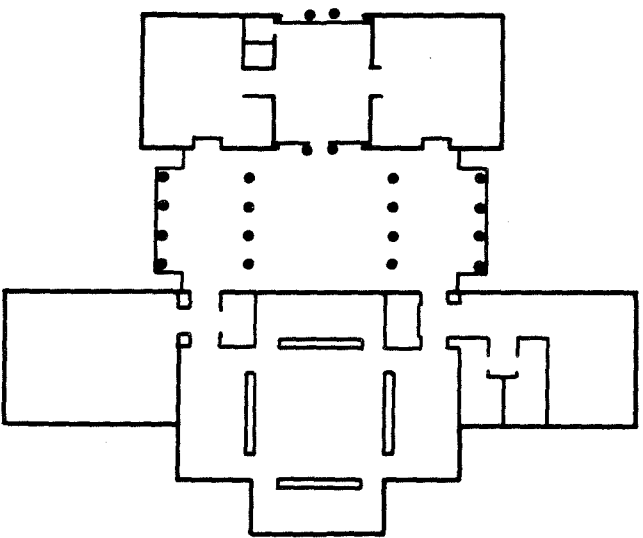
Figure 5

APPENDIX V

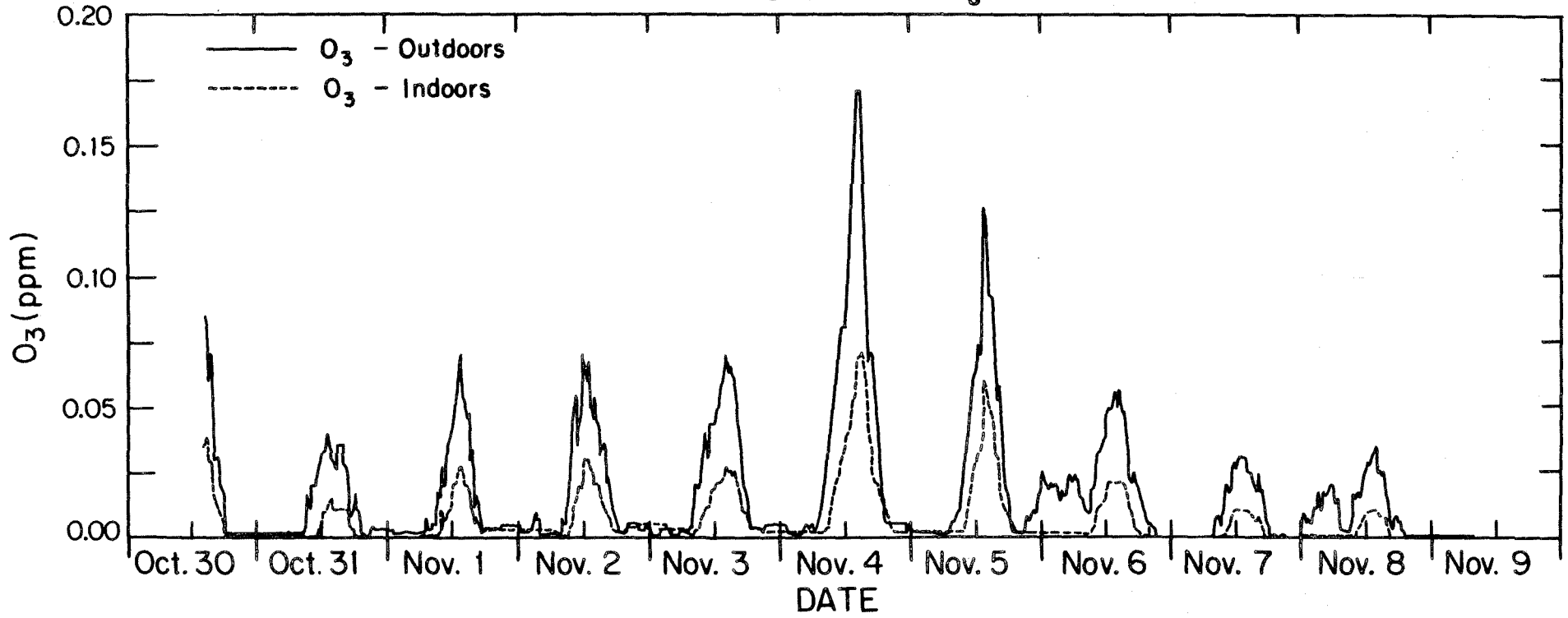
INDOOR/OUTDOOR RELATIONSHIPS
FOR O_3 , NO and NO_2 AT THE
VIRGINIA STEELE SCOTT GALLERY,
HUNTINGTON LIBRARY, SAN MARINO

**VIRGINIA STEELE SCOTT GALLERY
HUNTINGTON LIBRARY, SAN MARINO**

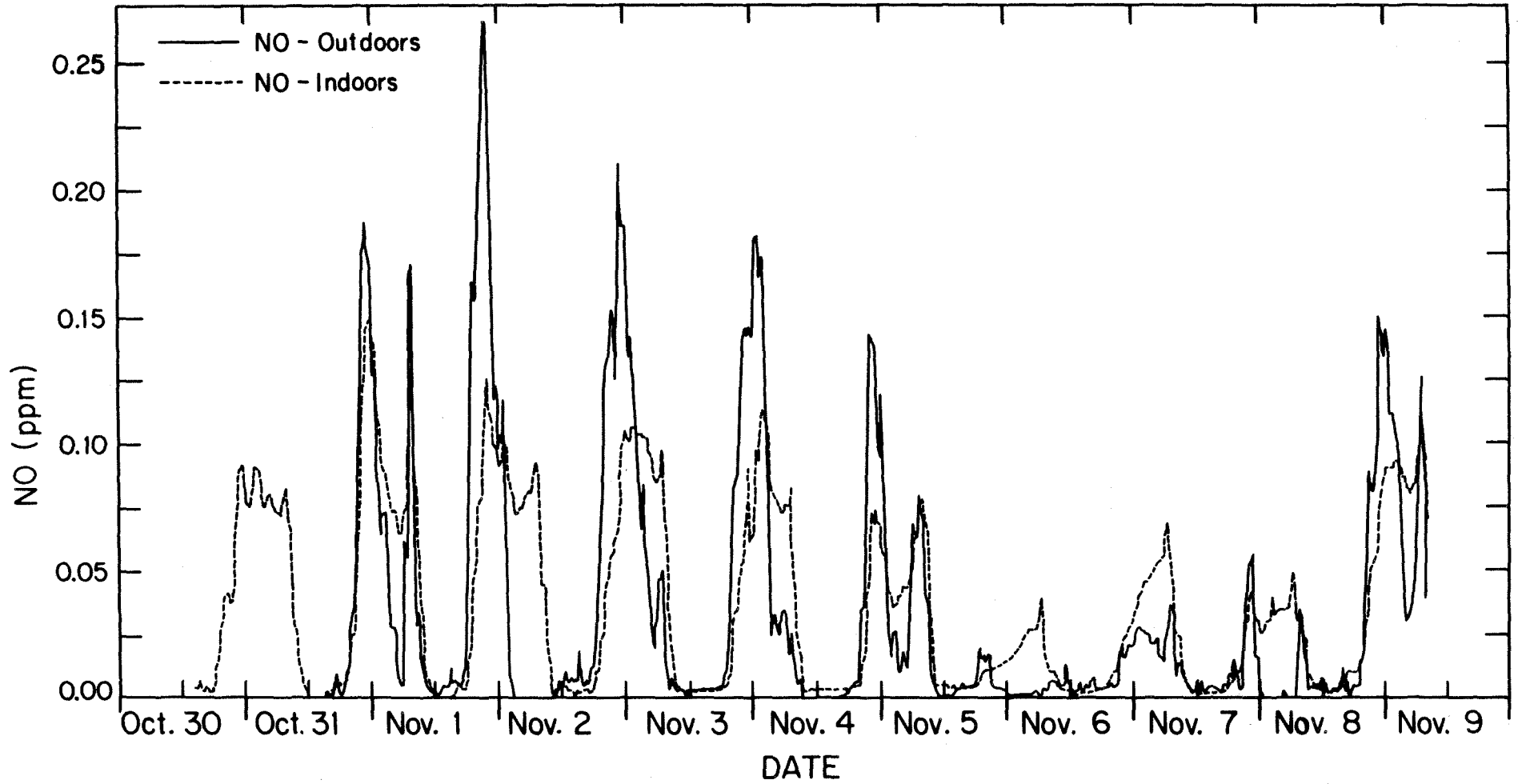
(air conditioned but no activated carbon filtration)



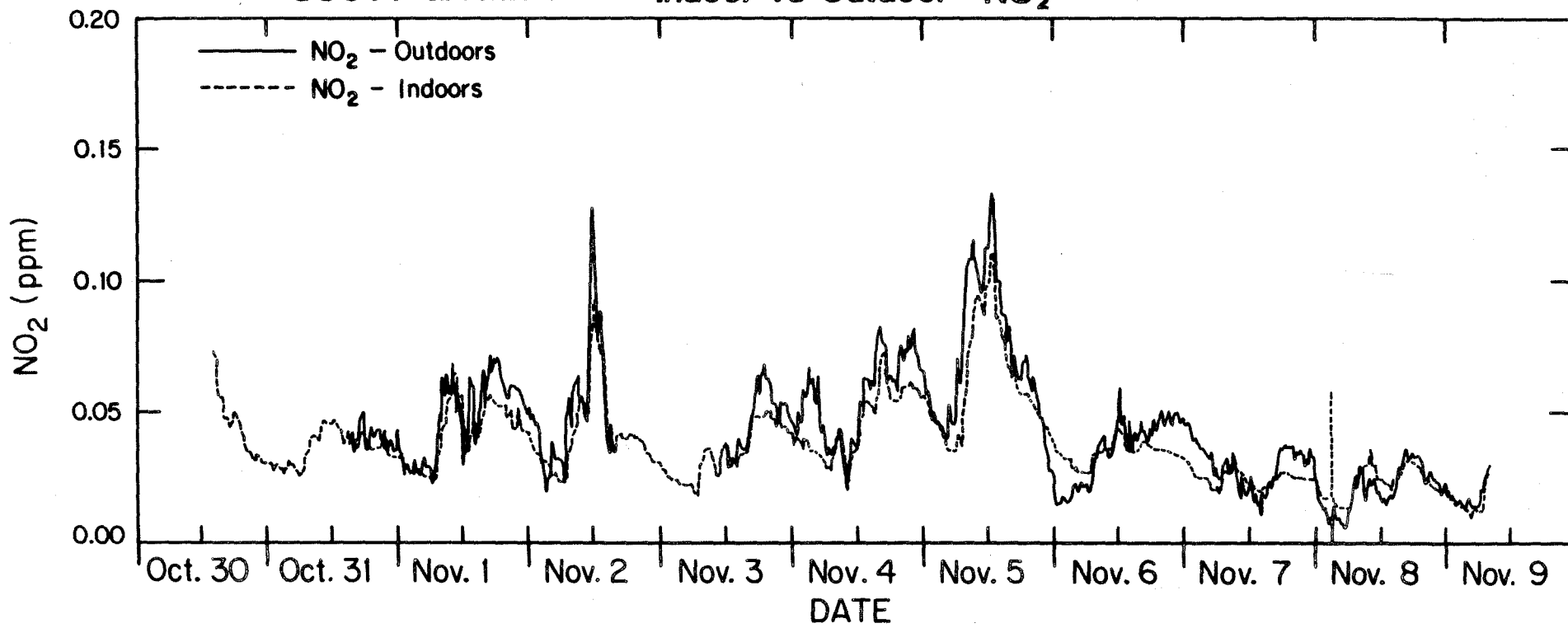
SCOTT GALLERY — Indoor vs Outdoor O₃



SCOTT GALLERY — Indoor vs Outdoor NO



SCOTT GALLERY — Indoor vs Outdoor NO₂



**COMPARISON OF INDOOR vs. OUTDOOR POLLUTANT CONCENTRATIONS
IN THE VIRGINIA STEELE SCOTT GALLERY**

<u>POLLUTANT</u>	<u>INDOOR AVERAGE (ppm)</u>	<u>OUTDOOR AVERAGE (ppm)</u>	<u>INDOOR AS PERCENTAGE OF OUTDOOR CONCENTRATION</u>
O ₃	0.0069	0.0178	39 %
NO	0.0369	0.0363	102 %
NO ₂	0.0384	0.0437	88 %

**PEAK 12 MINUTE AVERAGE POLLUTANT CONCENTRATION
VIRGINIA STEELE SCOTT GALLERY
OCTOBER 30 — NOVEMBER 9, 1984**

<u>POLLUTANT</u>	<u>INDOOR PEAK (ppm)</u>	<u>OUTDOOR PEAK (ppm)</u>
NO	0.150	0.267
NO ₂	0.111	0.134
O ₃	0.070	0.170