



## **Protection of Archival Record From Pollutants**

### **The Measurement of the Diffusion of SO<sub>2</sub> Through and Absorption of SO<sub>2</sub> By Archival Boxboard**

**Charles M. Guttman  
Kenneth L. Jewett**

U.S. DEPARTMENT OF COMMERCE  
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and Technology  
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Laboratory  
Polymers Division  
Gaithersburg, MD 20899

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## ABSTRACT

The diffusion and absorption properties of boxboards, commonly used to store archival documents, with sulfur dioxide have been measured.

For the most common boxes used by National Archives and Record Administration (NARA) a diffusion constant of about  $0.001 \text{ cm}^2/\text{sec}$  is measured for  $\text{SO}_2$  in the concentration range 10 ppm to 150 ppm. For this 15 fold change in gas concentration the calculated diffusion constant is found to be almost independent of gas concentration.

These results are discussed in terms of Passaglia's model of the microenvironment provided by these boxboards as used in archival storage.

Uptake of sulfur dioxide by boxboard was found to be very dependent upon the nature of the boxboard sample. Both permanent and nonpermanent binding of  $\text{SO}_2$  were observed and the contribution of each to the absorption of storage containers is discussed.



## FOREWORD FROM NARA

This report is the second in a series on research to investigate microenvironments, carried out by the National Institute of Standards and Technology for the National Archives & Records Administration (NARA). The genesis of this work was the report, "The Characterization of Microenvironments and the Degradation of Archival Records: A Research Program" by Elio Passaglia. This report suggested that in order to gauge the protection that boxes afford their contents, the diffusion and absorption properties of these boxes with respect to common indoor pollutants should be measured. The resulting report examines the diffusion and absorption properties of two boxboards used at NARA with respect to SO<sub>2</sub>. The two boxboards studied are not the only boxboards in use at NARA, and shouldn't be construed as being representative of commercially available boxboards, although they may be. They were simply materials received to test under two different NARA specifications (i.e. the Specification for Boxes: Archival, Acid Free, Metal Edge and the Specification for Boxes: Archival, Low Lignin, Metal Edge).

Also the study indicates that, at least from the standpoint of SO<sub>2</sub> absorption, the two boards show quite different capacities. Because these are two different boards, from two different paper mills, attributing this difference to one obvious difference in these two boards without further research would be unwarranted. Further, this study dealt only with the absorption of the pollutant SO<sub>2</sub> by the boxboards, which appeared, for the short term, at least, to be partially reversible in each board. Therefore, one should not conclude that the alkaline reserve in the boards doesn't protect the boxes or the records within from degradation by indoor air pollutants. Much evidence exists to attest to the beneficial effects of alkaline reserve in papers and board. It would be unwarranted and possibly hazardous to conclude that since it didn't appear to react with the SO<sub>2</sub> in this series of experiments it might well be omitted from board manufacture.

## TABLE OF CONTENTS

1.0	Introduction.....	1
2.0	Diffusion of SO <sub>2</sub> through archival boxboards.....	2
2.1	Diffusion experimental.....	2
2.1.1	Chemicals and materials.....	2
2.1.2	Apparatus.....	2
2.1.3	Porosity determinations through boxboards.....	2
2.2	The measurement of diffusion constant.....	3
2.2.1	Design of apparatus and calculations of diffusion constants.....	3
2.2.2	Effect of the boundary condition on the value of the diffusion constant.....	4
2.2.3	Achievement of the steady state condition.....	5
2.3	Results and discussion.....	5
2.3.1	Effects of SO <sub>2</sub> concentration on diffusion constant....	5
2.3.2	Porosity effects on diffusion constants for SO <sub>2</sub> through boxboards.....	5
2.3.3	Effect of composite nature of boxboard on diffusion constant.....	6
2.3.4	Comparison to earlier data.....	8
2.3.5	Comparison through the walls of box material to diffusion through gaps.....	8
3.0	Absorption of SO <sub>2</sub> by archival boxboard.....	10
3.1	Experimental.....	10
3.1.1	Chemicals and materials.....	10
3.1.2	Apparatus.....	10
3.2	Consideration on the design of experiments to determine the pickup of SO <sub>2</sub> by boxboard.....	10
3.2.1	Analytical considerations in the design of the flow-by absorption apparatus.....	11
3.2.2	Design of decay experiments.....	12
3.2.3	Use of dP/dt data.....	12
3.3	Total mass pickup data for SO <sub>2</sub> absorption by boxboard.....	12
3.4	Analysis of absorption results.....	13
3.5	Nature of SO <sub>2</sub> binding to boxboard.....	14
4.0	Conclusions.....	15
5.0	References.....	16
5.1	Acknowledgements.....	17
6.0	Figure captions.....	18

## 1.0 INTRODUCTION

Archives, libraries, and museums are involved in long term storage of records. Protecting these documents from degradation is a matter of great concern. Because temperature and atmospheric conditions in storage areas are important in mediating the rate of degradation of the stored records, temperature and humidity are controlled. However, atmospheric pollutants such as particulate matter, various oxides of nitrogen, sulfur dioxide (SO<sub>2</sub>) and ozone cause degradation of records (1). In some cases the removal of air pollutants from the external air by the air conditioning system is inefficient (2).

In storage areas such as stacks, many records are often kept in containers, and not exposed directly to the stack environment. These records experience a "microenvironment" which may be different from the macroenvironment of the stacks. If this microenvironment in fact is, or could be made to be, less aggressive, then expensive changes in the air conditioning system might be obviated.

Recently, Passaglia (3) studied this microenvironment with specific reference to storage in the National Archives and Record Administration (NARA). He suggested that a study of the protection mechanism provided by the container, in particular the cardboard boxes used to safeguard a large quantity of archival material, would be valuable. Passaglia presented models and calculations to estimate the effectiveness of various containers for protection of archival materials from environmental pollutants. However, in order to utilize these models, values of the adsorption and diffusion constants of the pollutants in archival boxboard is needed.

Herein, we report the measurement of the absorption and diffusion of sulfur dioxide in various boxboard materials used commonly to make storage boxes. Using these measurements along with Passaglia's model, we are able to ascertain the effectiveness of the archival boxes in providing a microenvironment that is different from the stacks.

This report is separated into two main sections. Treatment of diffusion experiments is discussed in Section 2.0 and subsections therein. Treatment of absorption data is handled in Section 3.0 and subsections therein. Conclusions for both sections are reported together in Section 4.0.

## 2.0 DIFFUSION OF SO<sub>2</sub> THROUGH ARCHIVAL BOXBOARD

### 2.1 Experimental

2.1.1 Chemicals and materials. Cylinders of 10 to 500 ppm concentrations of SO<sub>2</sub> in air were obtained from commercial sources and used as received. Calibrations were performed using those cylinders or SO<sub>2</sub> gas permeation tubes. Boxboard samples were obtained from NARA and Conservation Resources International.<sup>1</sup> Table 1 gives the detailed description of these boxboards.

2.1.2 Apparatus. Diffusion measurements were performed using the apparatus shown in Figure 1. SO<sub>2</sub> at a concentration of C<sub>i</sub> in air was passed through the top compartment while air was passed through the bottom compartment. Both gases were prehumidified by passing them through water solutions slightly acidified with sulfuric acid and maintained at 10.5 °C. Thus these gases contained relative humidities of about 50% at ambient conditions.

Sierra Instruments Model 840 flow controllers were used to control flow rates in the diffusion experiments and also to deliver accurately the desired gas flow rates when performing calibrations using SO<sub>2</sub> gas permeation tubes.

Sulfur dioxide concentrations were measured using a Hewlett Packard Model 5730A gas chromatograph with a sulfur-selective flame photometric detector, GC-FPD. A Supelco Chromosil 330 (1/8" x 8' teflon) column was used to verify that there were no other sulfur-containing gases present. Quantitative measurements were then made with a short length of 1/8" teflon tubing containing no packing material. This latter condition provided far greater measurement precision.

When the apparatus was clamped as shown in figure 1, the unsealed boundary condition (see Section 2.2.2) is obtained. The sealed boundary condition is obtained by additionally placing a bead of GE Clear RTV Silicone Rubber Adhesive Sealant around the circumference of the boxboard (D) seal with the stainless steel flange (F). Then all the boxboard extending beyond the lip of the flange was covered with an additional 8 mm of the sealant. The sealant was allowed to cure while gas flowed on both sides of the sample. On curing the sealant gives off acetic acid. High

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<sup>1</sup>Certain suppliers of chemicals and equipment are identified by name in order to specify the experimental conditions adequately. This does not imply endorsement or recommendation by the National Institute of Standards and Technology nor does it imply that the particular brands of chemicals and equipment named are necessarily the best for the purpose.

concentrations of acetic acid showed no signal in the GC-FPD detector. No sulfur-containing gases were found in samples collected from around the sealing region outside the apparatus.

2.1.3 Porosity determinations for boxboards. Paper and boxboard are porous materials. The fraction of the volume of the paper or boxboard which is in pores affects the diffusion rate through the boxboard. These effects will be discussed in a later section. This section discusses our estimate of the volume available to pores.

The volume of pores available to the gases in each paperboard is estimated by measuring the volume of a liquid picked up by the paperboard. This liquid, hexadecane, has a low surface tension and does not change the dimensions of the paperboard. A rectangular section of boxboard was weighed and its length, width, and thickness were measured. The sample was then immersed in hexadecane. While in a desiccator, vacuum was applied to the solvent-soaked boxboard sample. When bubbles no longer evolved from the hexadecane or the boxboard, the sample was removed, patted dry with paper towels, and weighed again. The dimensions were then remeasured to insure that no swelling due to the solvent had occurred. The porosity,  $P$ , was estimated

$$p = \Delta m / \rho_H V_p \quad (2.1)$$

where  $\Delta m$  is the mass of hexadecane picked up in the experiment,  $\rho_H$  is the density of hexadecane (taken to be 0.77) and  $V_p$  is the volume of the boxboard. The sample was then allowed to sit in an evacuated desiccator in the hexadecane for a few hours again and the measurements remade. No significant change was found in the amount of absorbed hexadecane.

## 2.2 The measurement of diffusion constant

2.2.1 Design of apparatus and calculations of diffusion constants. Diffusion measurements were made following the general design used in obtaining diffusion constants for gases in porous media (5). In these experiments a feed gas containing a fixed concentration of pollutants in air (50 % relative humidity [RH]) was passed on one side of the boxboard. On the other side of the sample only humidified air was passed as a sweep gas. The concentration of pollutant in each chamber was measured using a GC-FPD sensitive to sulfur. Figure 1 shows the design of the diffusion cell.

The diffusion constant may be determined as follows. The flux of the pollutant across the paper (5,6,7) is indicated by the following expression:

$$J_p = A D (dC/dx)_L \quad (2.2)$$

where  $J_p$  is the flux of the pollutant across the boxboard,  $A$  is the cross sectional area of the boxboard exposed to the gas,  $D$  is the diffusion constant and  $(dC/dx)_L$  is the change in concentration of  $SO_2$  in the boxboard at the air-boxboard interface in the bottom of the apparatus (see figure 1). The flux may also be expressed by

$$J_p = q_o C_o, \quad (2.3)$$

where  $C_o$  is the concentration of  $SO_2$  in the outlet side of the chamber where air is introduced and  $q_o$  is the flow rate of gas in that chamber. If we assume that at steady state the concentration across the paper is linear (8) then,

$$A D (dC/dx)_L = A D (C_i - C_o)/L, \quad (2.4)$$

where  $C_i$  is the concentration of  $SO_2$  on the bottom compartment of the apparatus and  $L$  is the thickness of the boxboard. Therefore,

$$D = (L/A) q_o (C_o/(C_i - C_o)). \quad (2.5)$$

In equation 2.4, the derivative  $(dC/dx)_L$  is taken inside the matrix. For a non porous medium a Henry's law solubility coefficient,  $S$ , relating the concentration of  $SO_2$  in the gas phase to its solubility in the medium multiplies both  $C_i$  and  $C_o$  (7,8). No treatment of diffusion through a porous medium in which there is partitioning of the gas into the matrix was found. Our measured diffusion constant may, therefore, be an apparent diffusion constant. Since the rate of change of concentration of  $SO_2$  in the stacks surrounding archival boxes is expected to be slow (1,3), our apparent diffusion constant is a good measure of diffusion of pollutants into archival boxes.

Sulfur dioxide diffused through boxboards G, H, and J so slowly that a diffusion constant could not be determined in our apparatus. However, the smallest concentration we could have measured may be estimated by using the GC-FPD calibration curve for  $SO_2$ . For  $SO_2$  at 147 ppm in air this concentration gives a value of 0.0025 for  $C_o/(C_i - C_o)$  in equation 2.5. For a value of  $q_o$  of 10 mL/min using a 60 point boxboard the smallest diffusion constant we can determine by our measurement technique is  $2 \times 10^{-5}$  cm<sup>2</sup>/s. The diffusion constants of boxboards G, H, and J must be less than this value.

Since  $SO_2$  is absorbed by paper (9), one might be concerned that no  $SO_2$  was observed through boxboards G, H, and J due to the massive absorption of  $SO_2$ . Concentration of the gas before it impinged on the boxboard ( $C_B$ ) was routinely measured. This measurement was made to check the calibration on the GC-FPD and the mass balance in the system. During the measurement of boxboards G, H and J, the

concentration of analyte entering and leaving the top chamber was not significantly different from  $C_b$ . If significant absorption of  $SO_2$  had occurred, a large concentration drop would have been expected.

2.2.2 Effect of the boundary condition on the value of the diffusion constant. Diffusion constants are obtained from experiments by assuming the measurements have been made on a sheet of infinite dimensions. Experimentally, that condition cannot be obtained. When diffusion through a finite area is measured, diffusion through the edges must be considered.

The boundary condition used in many diffusion experiments is one where the edges of the apparatus are sealed, thereby eliminating flux in that direction (8,10). Barrer et al. (10) discussed the error made by this boundary condition. For this current work, several measurements under this condition were performed. Under our experimental conditions Barrer's modeling (10) suggests that using this boundary condition leads to a diffusion constant that is no more than 8% higher than the diffusion constant obtained for infinite sheet case.

Measuring the diffusion constants in an apparatus that allows the sides of the boxboard to remain open is another boundary condition. Under this latter condition mass is lost through the edge, thereby reducing the flux into the bottom compartment. The quantity of mass lost can depend on the effectiveness of the clamping. This can vary from sample to sample. In the unsealed case, the measured diffusion constant is expected to be lower than the diffusion constant found in the sealed case. The data in Table 2 confirms that expectation.

The true (infinite sheet) diffusion constant lies between those found under these two boundary conditions. We feel that the data from the sealed case is a better representation of the true diffusion constant since its value varies only slightly from the infinite sheet value. However data from either case of sealing shows that the diffusion constant for the NARA boards is on the order of magnitude of  $0.001 \text{ cm}^2/\text{s}$ .

In Table 2, the diffusion constant obtained for various boxboards at 147 ppm  $SO_2$  in air is given for these boundary conditions. The effect of boundary conditions on our measurement is generally less than 20%.

### 2.2.3 Achievement of steady-state condition

All diffusion constants are obtained after steady state has been reached. Normally the experiment is started approximately 24 hours before data collection is initiated. Points are then

taken regularly two or three times daily. Steady state is assumed when the value of the diffusion constant shows no drift with time for at least 36 hours. Measurements obtained under these conditions eliminate all absorption interferences.

## 2.3 Results and discussion

2.3.1 Effect of SO<sub>2</sub> concentration on diffusion constant. The diffusion constants for two types of NARA boxboards at different SO<sub>2</sub> concentrations are summarized in Table 3. If one focuses on either the data of sample A or sample B, there are only small differences in the diffusion constants over a 14 fold change in a gas concentration. In fact, only the data on the 10 ppm point for the boxboard designated as B would suggest that there may be a concentration dependence beyond the repeatability error reported in the table. The measurement of the bottom at this low concentration required that we use much larger volumes of sample to get reliable signals on the FPD detector. This change may introduce a systematic error not reflected in the repeatability error.

These results suggest that the limiting low concentration diffusion constant of SO<sub>2</sub> in these boxboards may be close to the values of the diffusion constant reported herein. Thus, these data and previously mentioned observations tend to provide confidence for the experimental approach used in this study.

2.3.2 Porosity effects on diffusion constants for SO<sub>2</sub> through boxboards. Data from porosity experiments are summarized in Table 4. Whereas significant sample weight gains were measured, the dimensions of paperboard samples remained unchanged. Therefore, it appears that the hexadecane did not swell boxboard samples, but only entered the pores of samples.

Although the chemical composition of papers or boxboards may vary from one grade to another, the physical structure is always porous. Literature suggests that papers have pores from between 0.1 and 100 micrometers (12).

Porous catalysis is used in several chemical manufacturing processes. Diffusion through these catalysis, which are usually metal or ceramics, have been studied in great detail (5,13). In models of diffusion of gases through porous structures, diffusion of the gas through porous media is dominated by the diffusion of that gas through pores. Thus, for the random pore model (5), the diffusion constant of the pollutant in porous media is decreased by the volume available to the gas (i.e. the fraction of actual volume in the pores), and a tortuosity factor which describes the increased path length the gas must travel. These ideas are expressed as

$$D_p = D_g f_p / t_p, \quad (2.6)$$

where  $D_p$  is the diffusion constant of the pollutant gas in porous media,  $D_g$  is the diffusion constant of the gas in air,  $f_p$  is the fraction of volume of the paperboard in pores, and  $t_p$  is the tortuosity factor for the material.

Generally  $f_p$  is from 0.2 to 0.8. For boxboards without glue, samples D, E and F, and for the diffusion constant of rag paper (11),  $f_p$  ranges from 0.25 to 0.6. Literature values of  $t_p$  reported for catalysis range from about 1.0 to 100 (13). Diffusion data for Sample D, E and F suggest  $t_p$  values in to that range.

Diffusion data on eight boxboards are shown in table 5. The diffusion constant of these boxboards are plotted against porosity in Figure 2. According to the manufacturer, the boxboards D, E and F have no glue layer. For a given porosity, these boxboards have higher diffusion constants than the rest of the boxboards measured. This suggests that the glue may have an effect on the measured diffusion constant.

2.3.3 Effect of composite nature of boxboard on diffusion constant. Many of the boxboards used to make boxes for archival storage are composite boards, made up from thinner boards that are glued together. This glue layer may affect  $SO_2$  permeability through the boxboard. Two extreme cases may be considered. In one case the glue attaches to the matrix and does not fill or affect the pores. In the other case the glue creates a well defined intact polymer film with no holes between the two paperboards. In the first case,  $SO_2$  flux through the boxboard is not affected by the presence of the glue. In the latter case, the glue may completely control the flux.

Boxboard H is a composite board manufactured by gluing three layers of boxboard F together. The manufacturer of the boxboard claims that there is about 4.5 kilograms of dry adhesive left per 280 square meter of boxboard laminated. Assuming the density of the dry adhesive is one gm/cc, we estimate a total thickness of adhesive of 0.0016 cm for the two glue films between the three pieces of boxboard.

For a composite board the diffusion constant may be estimated from the diffusion constant of its components as (8):

$$L/D = \sum l_i / D_i, \quad (2.7)$$

where the sum is over the constituents of the composite.  $l_f$  is the total thickness of the film (0.0016 cm) and  $l_b$  is the total thickness of boxboard (0.16 cm). From data reported herein, the diffusion constant of boxboard F,  $D_b$ , is 0.003  $cm^2/s$ . For  $D_f$ , the diffusion constant in the film, we assign a value of

$1.0 \times 10^{-8}$  cm<sup>2</sup>/s. This value is estimated from a literature value for various gases in PVA films (14). Then equation 2.7 becomes,

$$l_b/D = l_f/D_f + l_b/D_b, \text{ or} \quad (2.8)$$

$$0.16/D = .0016/(5 \times 10^{-9}) + .16/.003, \quad (2.9)$$

and therefore

$$0.16/D = 1.6 \times 10^5 + 567 \quad (2.10)$$

The dominance of the first term on the right-hand side shown in equation 2.10 should be noted. Even an order of magnitude variation in the boxboard diffusion constant would not change the impact of  $l_f/D_f$  dominance.

When equation 2.10 is solved, the diffusion constant for the composite board, sample H, is estimated to be  $1.0 \times 10^{-6}$ . This value is within our estimated bound for the diffusion constant of Sample H given in table 4.

If the glue film is not intact, the value of  $l_f/D_f$  could change by many orders of magnitude. This loss of total coverage by a film could arise in the original laying down and drying of the film or could result from the aging of the film. This may explain why some composite boards give the high diffusion constant, samples A, B, and C, and some very low, samples G, H, and J. Thus, the properties of the glue used to make up the boxboard must be considered when estimating the overall flux of pollutants through a boxboard whose diffusion constant has not been measured.

2.3.4 Comparison to earlier data. Dimitroff and Lacksonen (11) reported that the diffusion of sulfur dioxide in air through stacked layers of rag paper was 0.007 cm<sup>2</sup>/s. They measured a porosity of the rag paper of 25%. The value of the diffusion constant Dimitroff and Lacksonen obtain for paper is of the same order of magnitude as the values we obtain for various boxboards. However, their value of diffusion constant is higher than any value of diffusion constant obtained on boxboard in this work and their value of porosity is lower than any obtained in this work. Assuming the paper and boxboard have equivalent tortuosity factors, models of diffusion in porous media would suggest that the diffusion constants in papers with low porosities should be lower than those with high porosities.

Two comments about this apparent inconsistency are in order. First, Dimitroff and Lacksonen made their measurements on a stack of paper. The structure of the paper itself may be different enough from that of the boxboard that we measure to make such a difference in the diffusion constant. Furthermore, between each sheet is an air space. Sulfur dioxide diffuses through air faster

than it diffuses through paper. Thus, their measured value of diffusion constant of SO<sub>2</sub> in rag paper may be higher than the true value.

Second, they measure the diffusion constant by sealing the edges of their paper. This boundary condition leads them to measure fluxes through the paper that would be higher than would be measured in an infinite sheet. Barrer et al. (10) modeled the diffusion constant measurement in a sealed system and showed the errors made by this measurement compared to the infinite sheet measurement (see Section 2.2.2). Barrer et al. demonstrated that the error in the measurement is strongly dependent on the ratio of the thickness of the sample to the radius of the cross-sectional area through which the gas is passing. As this ratio increases, the error increases. Our interpretation of the Dimitroff and Lacksonen paper suggests that this ratio is about 0.4 for their measurements. In that case the Barrer et al. paper suggests the measured flux would be too high by at least 40%. This would result in a high apparent diffusion constant.

2.3.5 Comparison through the walls of box material to diffusion through gaps. Passaglia (3) studied the microenvironment provided by archival boxes in protecting their contents from atmospheric pollutants. In his model of the flux of pollutant through the box, Passaglia allowed for flux through the boxboard of the box and flux through the gaps or openings in the container (or box) walls. In that study he points to the importance of diffusion through gaps as a mode to bring stack pollutants into the archival box microenvironment. In his study, Passaglia assumed the boxboard had a diffusion constant of 10<sup>-8</sup> cm<sup>2</sup>/s. He concludes that the flux brought about by diffusion through gaps is much higher than the flux resulting from diffusion through the paperboard itself. This suggests that closing the gaps will result in better controlling the microenvironment.

Although his models are essentially correct, Passaglia had no measured values of the diffusion constants of pollutants through boxboard available to him. From the measurements provided in this work we find diffusion constants ranging from 10<sup>-3</sup> to 10<sup>-6</sup> cm<sup>2</sup>/s for the various measured boxboards. Following Passaglia's equation 2.8 the ratio of the concentration on the inside of the container, C<sub>1</sub>, to the concentration of pollutant outside the container, C<sub>2</sub>, for either flux through gaps, i = g, or through the boxboard, i = b, is given by

$$C_1/C_2 = 1 - (1 - C_1^0/C_2) \exp(-t/\tau_i) \quad (2.11)$$

where  $\tau_i = V_i l_i / (A_i D_i)$  for i = g for the gaps and i = b for the boxboard. Values for the values of V<sub>i</sub>, l<sub>i</sub>, A<sub>i</sub>, and D<sub>i</sub> used in figure 3 are given in table 6. Except for the value of the diffusion constant through boxboard these values are those given by

Passaglia. We have used a value of diffusion through boxboard ( $2.0 \times 10^{-3} \text{ cm}^2/\text{s}$ ), which is near that obtained for the two NARA boxboards. Figure 3 also includes a curve that shows the rate of uptake of the gases assuming a value of the diffusion constant of the boxboard of  $10^{-8} \text{ cm}^2/\text{s}$ . This value is close to the value Passaglia assumed.

With the value of the diffusion constant for boxboard in the range of the NARA boxboard value, we find that the total flux of  $\text{SO}_2$  through the boxboard is greater than the flux through gaps. Thus modifying the boxes so that the gaps are eliminated or made much smaller will not change the rate of exchange of pollutant between the outside and inside of the NARA boxes. However, for the boxboards with much smaller diffusion constants like those values found for samples of G, H, and J, there may be some advantage to sealing the gaps.

### 3.0 ABSORPTION OF $\text{SO}_2$ BY ARCHIVAL BOXBOARD

#### 3.1 Experimental

3.1.1 Chemicals and Materials. Cylinders of 10 to 500 ppm concentrations of  $\text{SO}_2$  in air were obtained from commercial sources and used as received. Calibrations were performed using those cylinders or  $\text{SO}_2$  gas permeation devices from VICI Metronics. Boxboard samples were obtained from NARA and Conservation Resources International. Two different boxboard samples were used in these experiments. Both types of samples were acid-free, but one sample was also a higher quality, low lignin boxboard.

3.1.2 Apparatus. Absorption measurements were performed using the apparatus shown in figure 4.  $\text{SO}_2$  at a concentration of  $C_m$  in air was passed through into the apparatus through A passing the boxboard. As the gas passed the paperboard it was absorbed and its concentration decreased. The concentration at the outlet side, B, was measured. The gas had been prehumidified by passing it through water solutions slightly acidified with sulfuric acid and maintained at  $10.5^\circ\text{C}$ . Thus the gas contained relative humidities of about 50% at ambient conditions.

Sierra Instruments Model 840 flow controllers were used to control flow rates in the absorption experiments and also to accurately deliver the desired gas flow rates when performing calibrations using  $\text{SO}_2$  gas permeation tubes.

Sulfur dioxide concentrations were measured using a Hewlett Packard Model 5730A gas chromatograph with a sulfur-selective flame photometric detector, GC-FPD. A Supelco Chromosil 330 ( $1/8" \times 8'$  teflon) column was used to verify that there were no other sulfur-containing gases present. Quantitative measurements were then made with a short length of  $1/8"$  teflon tubing containing no packing

material. This latter condition provided far greater measurement precision.

3.2 Consideration on the design of experiments to determine the pickup of SO<sub>2</sub> by boxboard. To obtain a proper estimate of the relevant constants, the SO<sub>2</sub> pickup as a function of time and concentration must be examined. These data may provide information on the mechanism of pickup of the pollutant by boxboard.

The major previous work on quantitative pickup of a pollutant by paper was performed by Hudson et al. (9). These researchers used a radiotracer technique to determine the amount of SO<sub>2</sub> picked up by the paper itself. This procedure is potentially the most direct method to measure SO<sub>2</sub> pickup. However, radiotracer techniques are not available for reaction systems involving, for example, NO<sub>x</sub> or ozone. Since these gases may also be important in future degradation studies, an experimental methodology which can be more universally applied was developed.

The apparatus which is described in this paper involves measuring the depletion of the pollutant in the gas phase due to boxboard absorption. Two experimental methods are described below in sections 3.2.1 and 3.2.2. For some absorption experiments, a flow-by absorption method was used when the rate of pickup is high. In these experiments, at low pickup rates, a measurement of the decay of the SO<sub>2</sub> concentration in a sealed container was used. In all other experiments the flow-by apparatus was employed alone.

3.2.1 Analytical Considerations in the design of the flow-by absorption apparatus. Sulfur dioxide at ppm concentrations in humidified air is sent through the absorption apparatus (figure 2) of volume, V<sub>c</sub>. The apparatus contains a paperboard sample of volume, V<sub>p</sub>, and mass, m<sub>p</sub>. Gas flows at a specific rate, q. The sample absorbs SO<sub>2</sub>, thereby decreasing the SO<sub>2</sub> concentration in the gas. The concentration of the SO<sub>2</sub> at the inlet is C<sub>m</sub> and that at the outlet is C<sub>o</sub>. Both are expressed in units of grams of SO<sub>2</sub> per cubic centimeter of air. The flux equation that describes this situation is,

$$J_{in} = J_{ab} + J_{out} , \quad (3.1)$$

where J<sub>in</sub> is flux in gms/s of pollutant flowing into the apparatus, J<sub>ab</sub> is flux of pollutant absorbed, and J<sub>out</sub> is the flux of pollutant exiting the apparatus. Furthermore,

$$J_{in} = q C_i , \text{ and} \quad (3.2)$$

$$J_{out} = q C_o , \quad (3.3)$$

where  $q$  is the flow rate of the carrier gas in cc/s. The absorption flux,  $J_{ab}$  is described by,

$$J_{ab} = m_p \, dP/dt, \quad (3.4)$$

where  $P(t)$  is the concentration of pollutant absorbed by all mechanisms in the paper at time  $t$  in gm of pollutant/gm paper, and  $m_p$  is the mass of the paper. Therefore, the rate of pickup of  $SO_2$  absorbed into boxboard by any mechanism,  $dP/dt$ , is shown in equations 3.5 and 3.6.

$$dP/dt = (q/m_p) (C_m - C_{out}) \quad (3.5)$$

$$dP/dt = (C_m/m_p) (q(1-C_{out}/C_m)) \quad (3.6)$$

As we shall describe in section 3.2.2, in the first experiments of this design we used a combination of a flow-by experiment and then a decay experiment. Using the pickup apparatus in this methodology we choose a mass of paper so that at 20 cc/minute flow rate we could obtain measurable  $C_{out}$  even at the earliest time (during the first hour of the experiment). Without good early time data we can not integrate the data to get total pickup. This meant we were limited to no more than 0.5 grams of paperboard in the reactor. At later times in the experiment, this small amount of paperboard limited the sensitivity in the flow-by experiment.

The above method allowed us to get a good measure of total pickup. However it limited our sensitivity at long times. To improve the sensitivity at long times, in later experiments we used a much larger piece of boxboard, up to 3.2 grams. In order to keep the  $C_{out}$  close to  $C_m$  even at early times in these experiments we varied the flow rate during a single experiment. In a given experiment the flow rate was as high as 100 cc/minute at early times and decreased to 4 cc/minute at later times. This allowed us to keep  $C_m$  close to  $C_{out}$  at early times in the experiment and to obtain much more sensitivity at low gas pickup,  $dP/dt$ , at later times in the experiment.

In a dynamic (flowing) situation only the concentration of the pollutant flowing in versus the concentration of pollutant flowing out needs to be measured. Using gas chromatography with a sulfur-specific flame photometric detector (GC-FPD), concentrations of  $SO_2$  described by  $(1 - C_{out}/C_m)$  may be measured down to a value of approximately 0.06 with an error of about  $\pm 0.02$  when  $C_m$  is between 10 and 300 ppm  $SO_2$ . Thus, we estimate we can measure a  $dP/dt$  value as low as  $3 \times 10^{-9}$  gm  $SO_2$  /gm paper/min at 60 ppm  $SO_2$  in air. This value is obtained by assuming a minimum flow rate as of 3 cc/min and a maximum sample weight of 3 grams. These parameters are the best that are attainable under the present set of experimental conditions. In most of the experiments reported herein,

measurements at higher flow rates and lower paperboard masses were made. Such conditions increase the limiting values for  $dP/dt$ .

3.2.2 Design of decay experiments. A mixture of  $SO_2$  is directed through an absorption cell (figure 4) containing a boxboard sample. When  $C_{in} = C_{out}$  at time  $t_f$ , the gas flow was stopped and the container sealed. The decay of  $SO_2$  concentration versus time was then monitored. Assuming no  $SO_2$  loss except to boxboard, mass balance inside the absorption apparatus may be written as follows:

$$V_g [G(t_f) - G(t_f + t)] = m_p [P(t_f + t) - P(t_f)], \quad (3.7)$$

where  $V_g$  is the volume (cc) of the reactor,  $G(t_f)$  is the  $SO_2$  concentration at the time that the gas flow was stopped and the container sealed, and  $G(t_f + t)$  is the concentration of  $SO_2$  at time  $(t_f + t)$ . By considering only the initial decay at time  $t_f$  then,

$$m_p (dP/dt)_{t_f} = V_g (dG/dt)_{t_f} . \quad (3.8)$$

If the initial slope of the decay in the reactor is measured, an estimate of  $dP/dt$  can be obtained. The flow-by experiment described in Section 3.2.1 obtains estimates for  $dP/dt$  after the gas has flowed for time,  $t_f$  while the decay experiment tries to measure the same quantity. In some experiments, flow-by measurements are made at early times when  $dP/dt$  is changing rapidly while the decay measurements are performed when  $dP/dt$  is changing slowly. In later experiments improvements in experimental design permitted the use of flow-by data at both early and later times.

3.2.3 Use of  $dP/dt$  data. From both of the previous descriptions of absorption experiments,  $dP/dt$  may be obtained. The value for  $P$  may be obtained by integration of  $dP/dt$  using the following expression:

$$P(t) = \int_0^t (dP/dt) dt. \quad (3.9)$$

### 3.3 Total mass pickup data for $SO_2$ absorption by boxboard

The total  $SO_2$  pickup by boxboard may be determined by integrating  $dP/dt$  over time. Figure 6 shows an example of this integrated data. Since measurements are made until  $dP/dt$  is zero by our experimental techniques, we feel our integrated data provides a good estimated of the total  $SO_2$  pickup by the boxboard. Table 7 shows data for experiments carried out with samples A and B as a function of concentration and mass of sample used. For both types of boxboard the total pickup per unit mass of boxboard is independent of flow rate and boxboard mass. This shows that the

measurement of total mass pickup does not depend on the way the experiment was run or on the mass of the sample.

We also see that SO<sub>2</sub> pickup at long times is independent of SO<sub>2</sub> concentration. This suggests that saturation of the boxboard with SO<sub>2</sub> must have been obtained. Thus, at these concentrations the SO<sub>2</sub> solubility constant in boxboard (the Henry's law constant) can not be estimated. Perhaps going to lower concentrations, will make this possible.

These findings contradict the earlier work of Hudson et al., who reported that the absorption of SO<sub>2</sub> by rag paper was linear at long times. In those experiments, saturation was never attained. Here, experimental sensitivity may be an important consideration. We have estimated our experimental sensitivity for dP/dt as  $4 \times 10^{-8}$  g SO<sub>2</sub> /g paper /min (see section 3.2.1) at 60 ppm SO<sub>2</sub>. This is little different from that of Hudson which we estimate from his figures as  $1 \times 10^{-7}$  g SO<sub>2</sub>/g paper /min at 100 ppm SO<sub>2</sub>.

Finally we see there is significant difference between the total mass pickup per mass of boxboard of sample B and sample A. Sample A has almost three times the absorption capacity as sample B.

### 3.4 Analysis of kinetics of the absorption results

In Section 2.0 diffusion constants for SO<sub>2</sub> in various boxboards were determined. Their values of approximately  $10^{-3}$  cm<sup>2</sup>/s suggest that absorption properties should be affected by diffusion phenomena during the first 10 minutes. Thus, the effects of the diffusion into porous media for the kinetic analysis of absorption data may be disregarded.

In order to describe the kinetics of absorption of SO<sub>2</sub> by boxboard using equation 3.5 or 3.6, C<sub>out</sub> must approach a somewhat steady percentage of C<sub>in</sub>. This condition was difficult to achieve during the initial phases of our earlier absorption experiments due to the extreme rapidity of absorption at these early times. As described in section 3.2.1 we have overcome some of these problems by varying the flow rate of the gas during the absorption runs.

Figures 6 and 7 illustrate a treatment of absorption data that meets the criteria for the ratio of C<sub>out</sub>/C<sub>in</sub> being fairly constant. During the first 10 hours of the experiment the value of dP/dt drops by a factor of 10. After approximately 100 hours, dP/dt approaches less the  $0.02 \times 10^{-6}$  g SO<sub>2</sub> /g paper/min, the limit of sensitivity for our experiments (see figure 7). The fact that after long times (dP/dt) does not achieve a constant value, suggesting there are no linear time dependencies at long times, contrasts with those results reported by Hudson et al. (9).

When  $P(t)$  is plotted against time the absorption levels off at long times to a steady state value. This is consistent with the observation that  $dP/dt$  vanishes at long times.

### 3.5 Nature of SO<sub>2</sub> binding to boxboard

Absorption may be a reversible or permanent phenomenon. Unlike reversible processes, i.e. gas chromatography, permanent absorption may involve chemical interactions between gas and solid substrates. These interactions will ultimately change the chemical form of the absorbed material thereby rendering it immobile. In the experiments reported herein, the fact that the  $dP/dt$  approaches zero suggests that all binding sites on the boxboard are filled.

Assuming fairly rapid ( $\leq 24$  hours) reaction to form permanently bound SO<sub>2</sub>, the following experiments were performed. Boxboards were exposed to SO<sub>2</sub> and gas uptake was measured. The gas was allowed to flow past the boxboard sample for at least 24 hours after  $dP/dt$  was found to be zero. Then the boxboard was removed from the absorption apparatus and allowed to sit in the room air for at least a week. Thus, the reversibly bound SO<sub>2</sub> was allowed to partition from the boxboard. The boxboard sample was then rerun.

The results of these determinations are presented in table 7 as experiment numbers 6 through 9. These data show a small decrease in the total pickup of boxboard B but a large decrease in the total pickup in boxboard A. This would suggest that there is more permanent binding for sample A than for sample B.

Figure 8 and 9 show these data as  $P(t)$  versus  $t$ . In both data sets, reabsorption results for at least the first up to 8 hours was unchanged from the respective original absorption experiments. This suggests that, for short durations, SO<sub>2</sub> is mainly reversibly bound to the boxboard substrates.

### 4.0 CONCLUSIONS

The diffusion constant of the common atmospheric pollutant, SO<sub>2</sub>, in the boxboards used to make up some archival boxes was determined to be 0.004 cm<sup>2</sup>/s and less. We suggest that although the diffusion in these boxboards appears to be close to that in a porous medium, the effect of glue on the diffusion constant is important. This layer of glue may be controlling the diffusion in some boxboards. We suggest that for those boxboards with diffusion constants in the range of .004 cm<sup>2</sup>/s that the total flux through a normal archival box is controlled by the diffusion through the boxboard, while for some of the boxboards with diffusion constants less than 10<sup>-6</sup>cm<sup>2</sup>/s we estimate the diffusion through the gaps dominate the flux through the walls of the box.

A method to measure the absorption of sulfur dioxide in boxboard has been developed. This method can be applied to any gas for which there is an analytical technique to accurately and quickly measure the concentrations of gas phase analytes. Taking into account the differences between Hudson's rag paper and the

boxboards used in these experiments, results of the two groups are comparable. However, the flow-by procedure described herein is generally more sensitive than the Hudson's static radiotracer method. For the boxboards analyzed in this report, the total amount of  $\text{SO}_2$  picked up is independent of the gas concentration for gases of 147 and 60 ppm in air. One board seems to show a significant permanent  $\text{SO}_2$  pickup after long time exposure to  $\text{SO}_2$ .

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## 6.0 FIGURE CAPTIONS

- Figure 1. Schematic of diffusion apparatus.  $\text{SO}_2$  in air at concentration  $C_i$  is flowed in at B. Air is flowed in at C.
- Figure 2. Plot of porosity versus diffusion constant for various boxboards.
- Figure 3. Ratio of the interior concentration,  $C_1$ , of an archival box to the concentration outside the box,  $C_2$ , as a function of time for an empty box for flow through gaps, for flow through box walls where the boxboard has a diffusion constant of  $10^{-8}\text{cm}^2/\text{s}$  or for flow through boxboard where the boxboard has a diffusion constant of  $2 \times 10^{-3}\text{cm}^2/\text{s}$ .
- Figure 4. Schematic of absorption apparatus.  $\text{SO}_2$  in air at concentration  $C_i$  is flowed in at D past the sample at G. In the flow-by design of this experiment, gas concentration is measured at  $A_1$  as  $C_m$  and at  $A_3$  as  $C_{out}$ . When the decay mode is used, both valves are closed and gas concentration is measured at  $A_2$ .
- Figure 5. Plot of total absorption,  $P$ , of  $\text{SO}_2$  by boxboard A at 147 ppm  $\text{SO}_2$  in air at 50% relative humidity as a function of time.  $P$  is in micrograms of  $\text{SO}_2$  per gram of boxboard.
- Figure 6. Plot of rate of absorption of  $\text{SO}_2$ ,  $dp/dt$ , by boxboard A under same conditions as figure 5.  $dp/dt$  is in micrograms of  $\text{SO}_2$  per gram of boxboard per hour.
- Figure 7. Data in figure 6 shown after 10 hours only.
- Figure 8. Plot of total absorption,  $P$ , of boxboard A by  $\text{SO}_2$  in air at 60 ppm and 50% rH and the reabsorption of  $\text{SO}_2$  by the same piece of boxboard after it was exposed to  $\text{SO}_2$ . See text for more detail.  $P$  is in micrograms of  $\text{SO}_2$  per gram boxboard.
- Figure 9. Plot of total absorption,  $P$ , of boxboard B by  $\text{SO}_2$  in air at 60 ppm and 50% rH and the reabsorption of  $\text{SO}_2$  by the same piece of boxboard after it was exposed to  $\text{SO}_2$ . See text for more detail.  $P$  is in micrograms of  $\text{SO}_2$  per gram of boxboard.

TABLE 1

SAMPLE ID	MEASURED AVERAGE THICKNESS in cm <sup>1</sup>	DESCRIPTION OF BOXBOARD <sup>2</sup>
A	0.144	60 pt, composite, acid-free, 3% CaCO <sub>3</sub> reserve, cut from NARA box
B	0.163	60 pt, composite, low-lignin, 3% CaCO <sub>3</sub> reserve pH 8.5, cut from NARA box
C	0.158	60 pt, composite, low-lignin, 3% CaCO <sub>3</sub> reserve, pH 8.5
D	0.0488	20 pt, lignin-free, 3% CaCO <sub>3</sub> reserve, pH 8.5, high-density
E	0.0235	10 pt, lignin-free, 3% CaCO <sub>3</sub> reserve, pH 8.5, high-density
F	0.0478	20 pt, lignin-free, 3% CaCO <sub>3</sub> reserve, pH 8.5, low-density
G	0.105	40 pt, composite, two pieces of D glued together
H	0.153	60 pt, composite, three pieces of F glued together
J	0.155	60 pt, composite, two E on outside glued to two F on inside

<sup>1</sup> On many boards we see point-to-point thickness variations of 10% when using a flat-head micrometer.

<sup>2</sup> Boxboards identified as composite are made by gluing thinner boards together.

TABLE 2

Effect of Apparatus Boundary Condition on  
Measured Diffusion Constant

Sample ID	Diffusion Constant ( $\text{cm}^2/\text{s}$ ) $\times 10^3$ at 147 ppm <sup>1</sup>	
	Sealed Edges	Unsealed Edges
A	1.13 $\pm$ 0.11	0.86 $\pm$ 0.05
B	1.92 $\pm$ 0.15	1.50 $\pm$ 0.21
D	3.20 $\pm$ 0.16	2.62 $\pm$ 0.05
E	0.62 $\pm$ 0.04	0.54 $\pm$ 0.04
F	3.24 $\pm$ 0.20	3.22 $\pm$ 0.09

<sup>1</sup> Relative humidity  $\approx$  50 %

Error estimates are one standard deviation of averages of repeated measurements.

TABLE 3

## Effects of Gas Concentration Diffusion Constant

Sample ID	Gas Concentration in ppm SO <sub>2</sub> in air	Diffusion Constant <sup>1</sup> , D x 10 <sup>3</sup> cm <sup>2</sup> /s
A	10.6	0.78 ± 0.11
A	60	0.91 ± 0.04
A	147	0.86 ± 0.05
B	10.6	1.10 ± 0.05
B	60	1.45 ± 0.04
B	147	1.50 ± 0.21

<sup>1</sup> All measured with unsealed edge condition  
Relative humidity  $\approx$  50 %  
Error estimates are one standard deviation of averages of repeated measurements.

TABLE 4

## Porosity and Density of Boxboards

Sample ID	Porosity	Density (g/cc)
A	0.55	.70
B	0.53	.74
C	0.51	.78
D	0.47	.84
E	0.38	.90
F	0.45	.66
G	0.46	.86
H	0.44	.73
J	0.50	.78

TABLE 5

Diffusion Constant of Various Boxboards  
at 147 ppm SO<sub>2</sub> in Air

Sample ID	Diffusion Constant <sup>1</sup> cm <sup>2</sup> /s x 10 <sup>3</sup>
A	1.13 ± 0.11
B	1.92 ± 0.15
C	0.42 ± 0.03
D	3.20 ± 0.16
E	0.62 ± 0.04
F	3.24 ± 0.20
G	< 0.02
H	< 0.02
J	< 0.02

<sup>1</sup> All measured with sealed edge condition  
Relative humidity  $\approx$  50 %  
Error estimates are one standard deviation of averages of repeated measurements.

TABLE 6

Parameters Used to Model a Typical Empty Container

---

Volume of box	11960 cm <sup>3</sup>
Area of box	3070 cm <sup>2</sup>
Thickness of wall	0.18 cm
Area of gap	7.6 cm <sup>2</sup>
Diffusion length in gap	3.3 cm
Assumed diffusion constant of SO <sub>2</sub> in air	0.2 cm <sup>2</sup> /s

TABLE 7

Pickup of SO<sub>2</sub> by Boxboard

Expt. #	Sample ID <sup>1</sup>	[Gas]ppm	Total Pickup, P, <sup>2</sup>	Flow Rate	Sample Mass
1	B	147	685	Fixed	0.51
2	B	147	756	Fixed	0.51
3	A	147	1833	Fixed	0.51
4	B	60	588	Fixed	0.51
5	A	60	1845	Fixed	0.50
6	B	60	668	Varied	1.00
7	A	60	1940	Varied	2.0
8 <sup>3</sup>	B	60	592	Varied	1.0
9 <sup>4</sup>	A	60	1200	Varied	2.0
10	B	147	684	Varied	3.2
11	A	147	1734	Varied	3.2

<sup>1</sup>See Table 1.

<sup>2</sup>Units of P are microgram SO<sub>2</sub>/g sample .

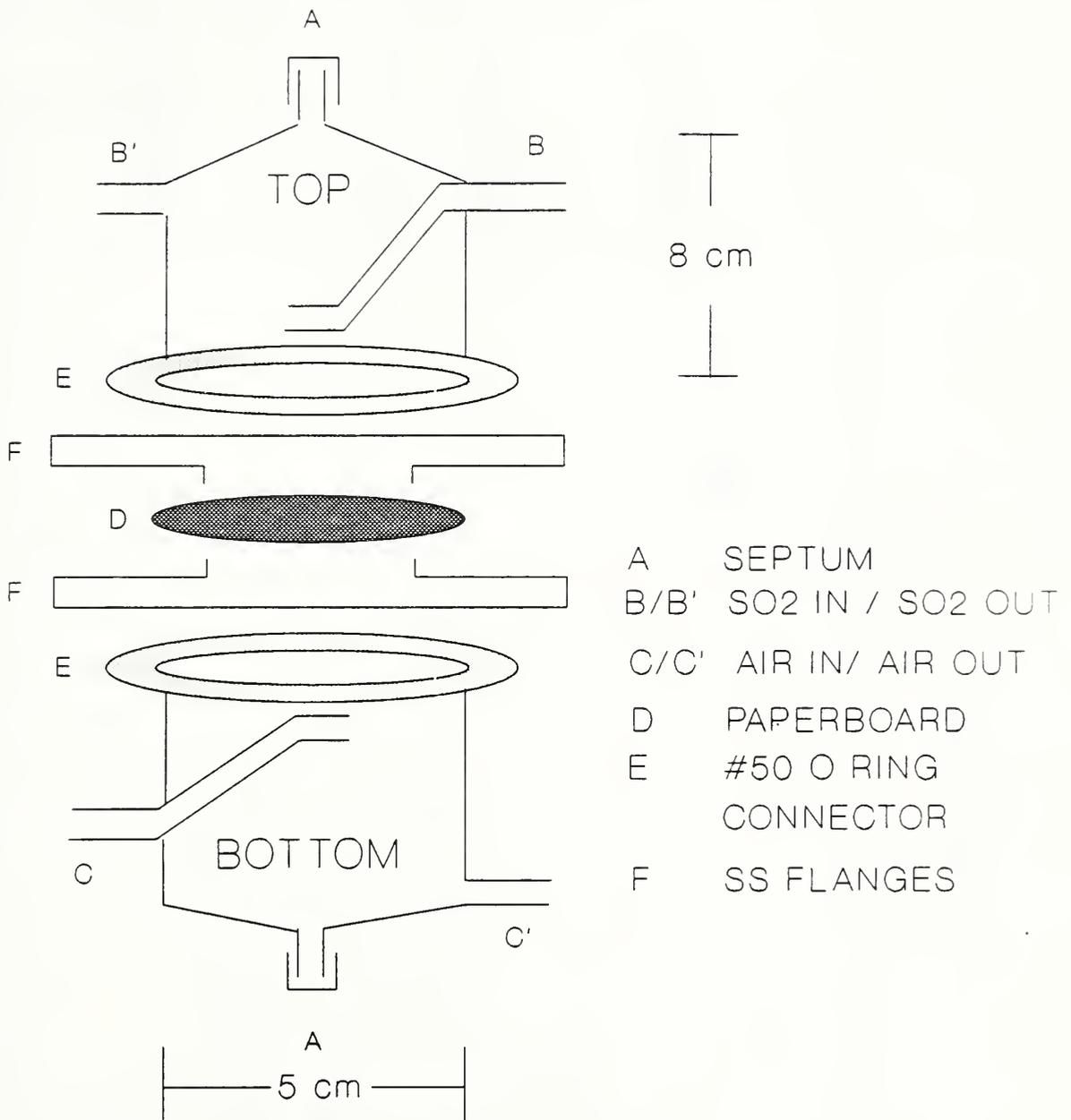
<sup>3</sup>Rerun of sample used in experimental 6.

<sup>4</sup>Rerun of sample used in experimental 7.



FIGURE 1

# DIFFUSION APPARATUS



## NOTES:

1. Contact area of paperboard = 3.14 cm<sup>2</sup>
2. All inlet and outlet tubing = 6 mm OD and 3 mm ID

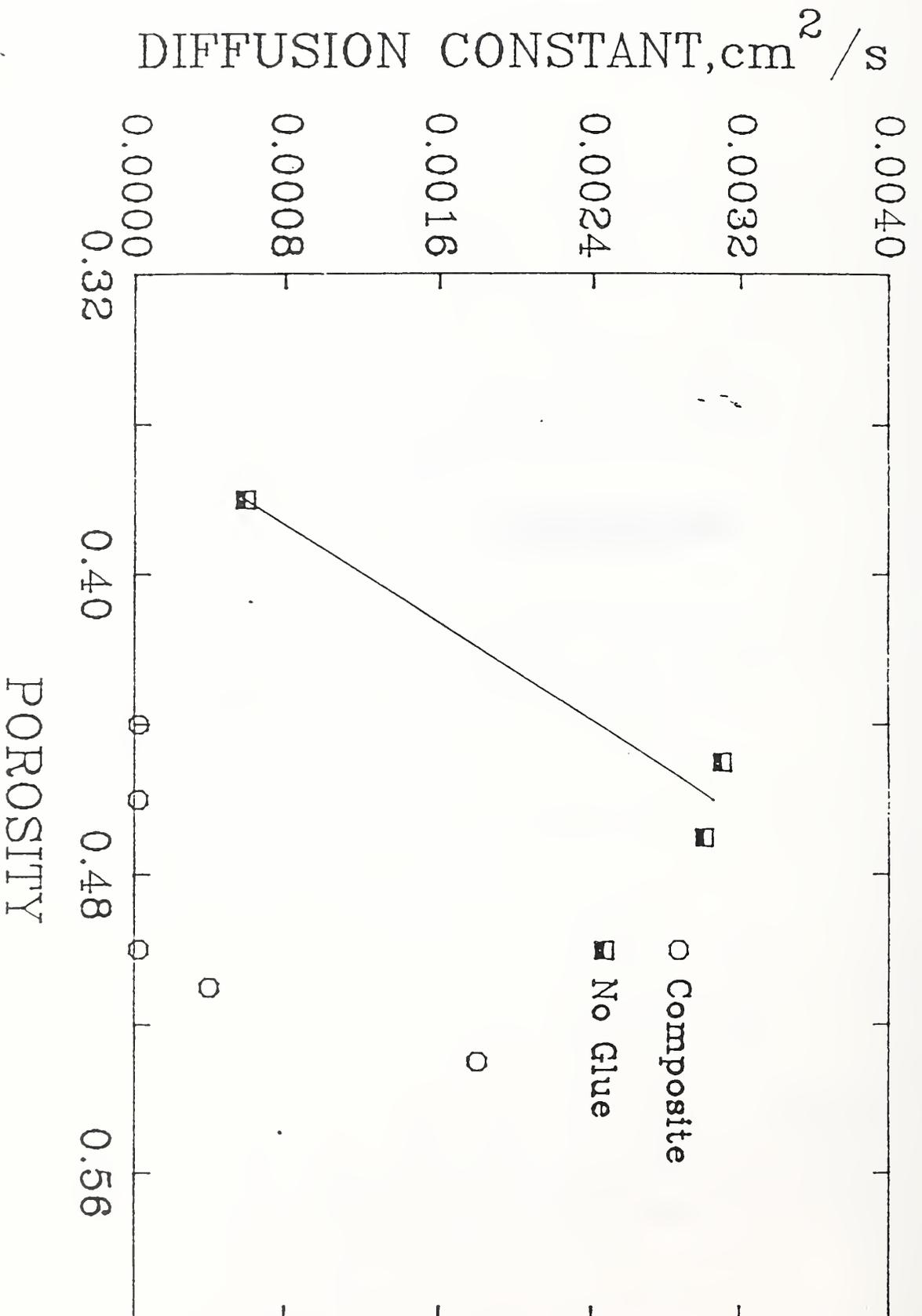


FIGURE 2

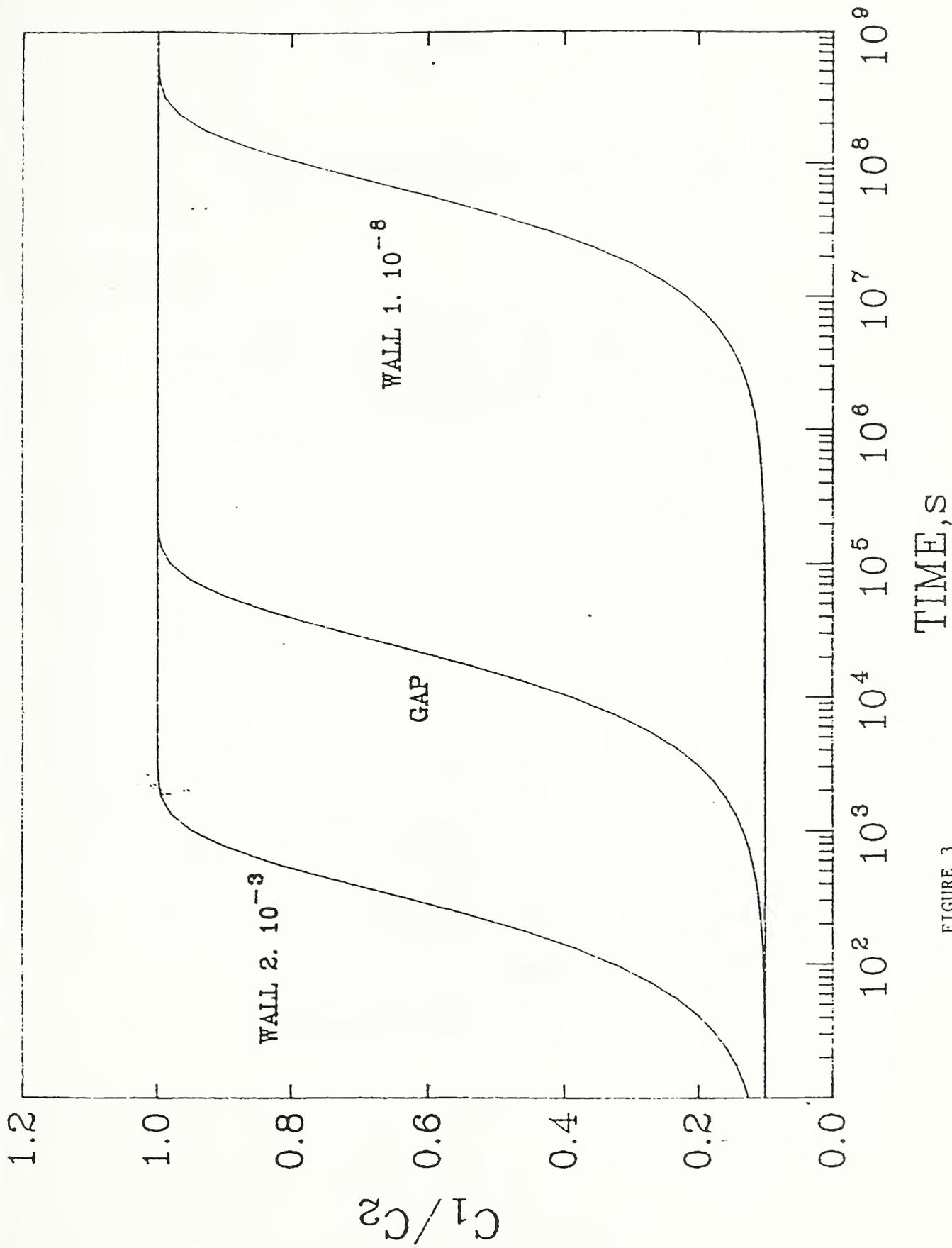
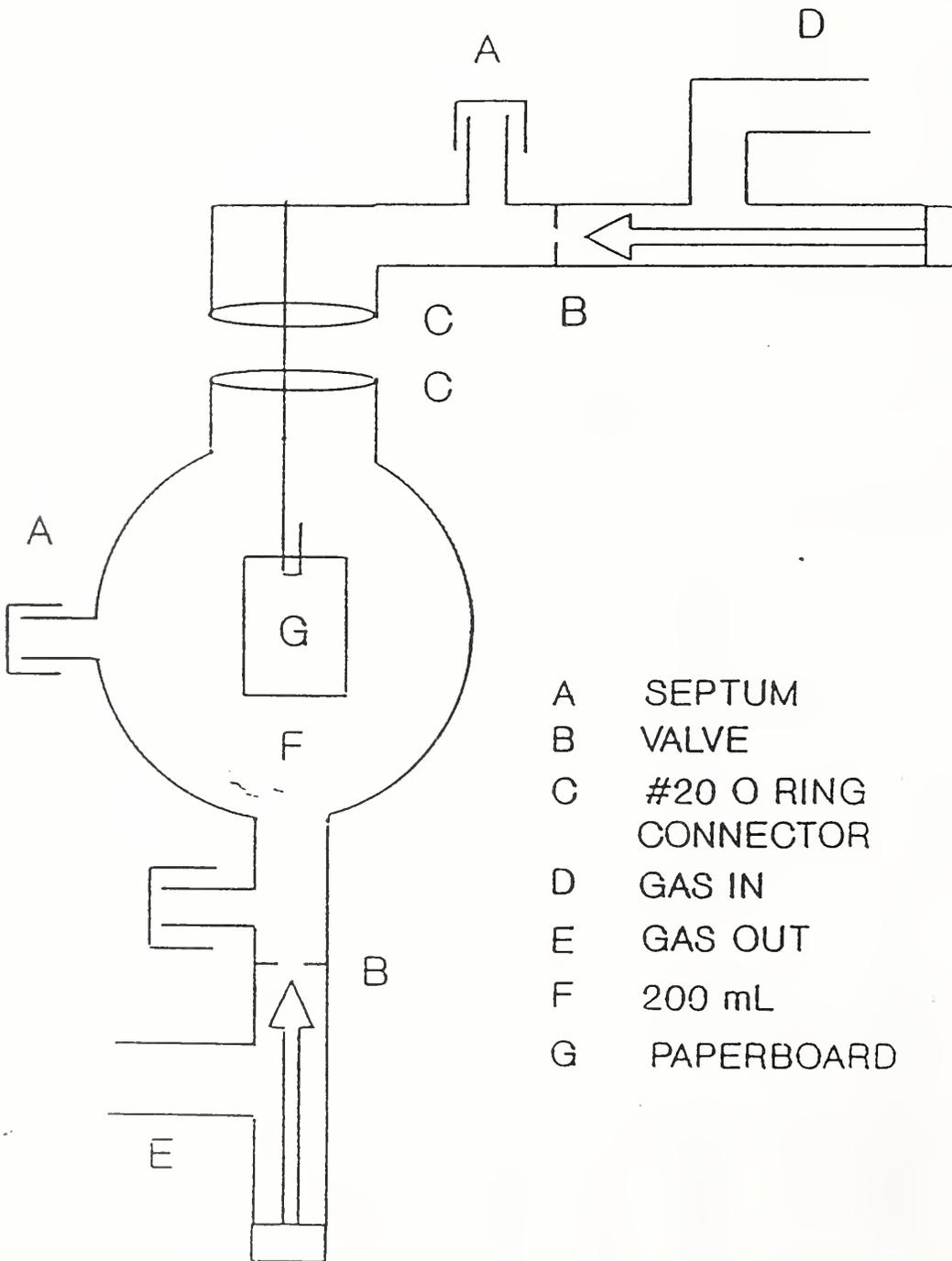


FIGURE 3

FIGURE 4

# ABSORPTION APPARATUS



- A SEPTUM
- B VALVE
- C #20 O RING CONNECTOR
- D GAS IN
- E GAS OUT
- F 200 mL
- G PAPERBOARD

FIGURE 5

# ABSORPTION IN BOXBOARD A

Gas 147 ppm

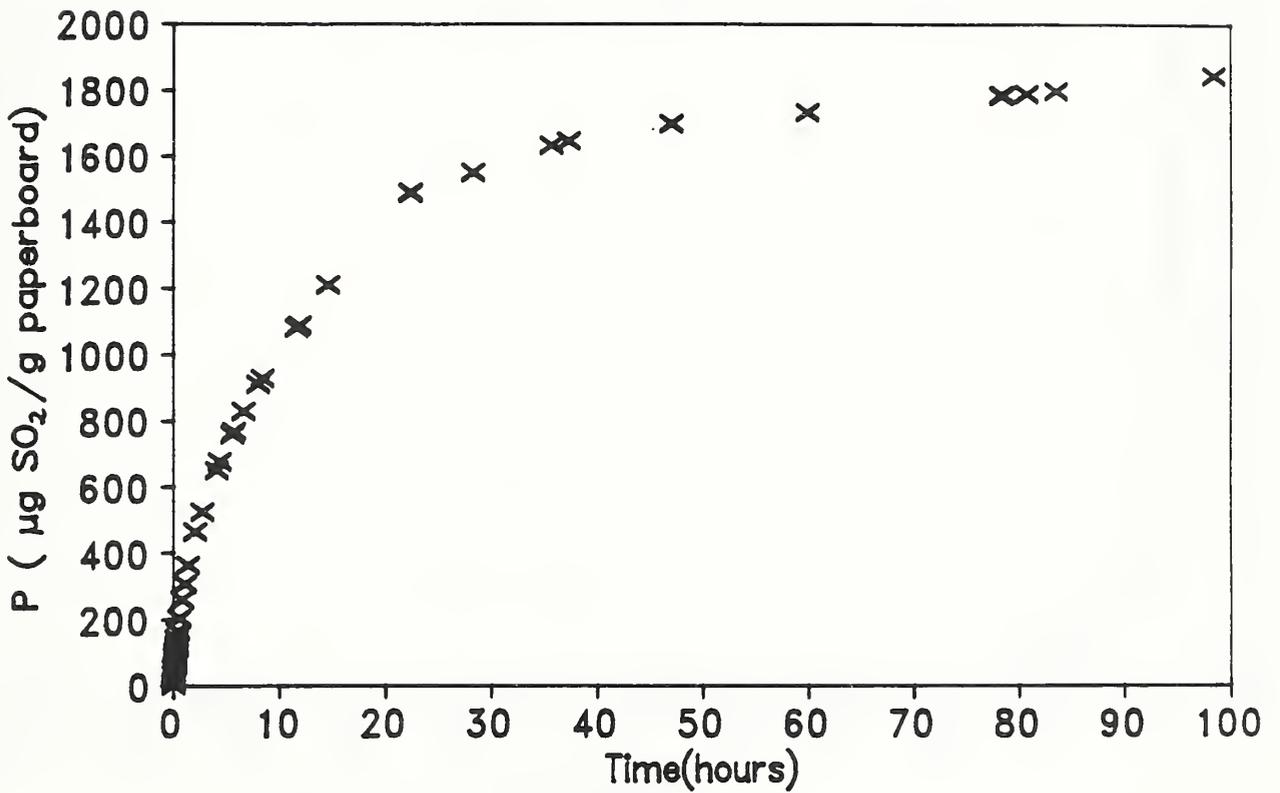


FIGURE 6

# ABSORPTION BOXBOARD A

Gas 147 ppm

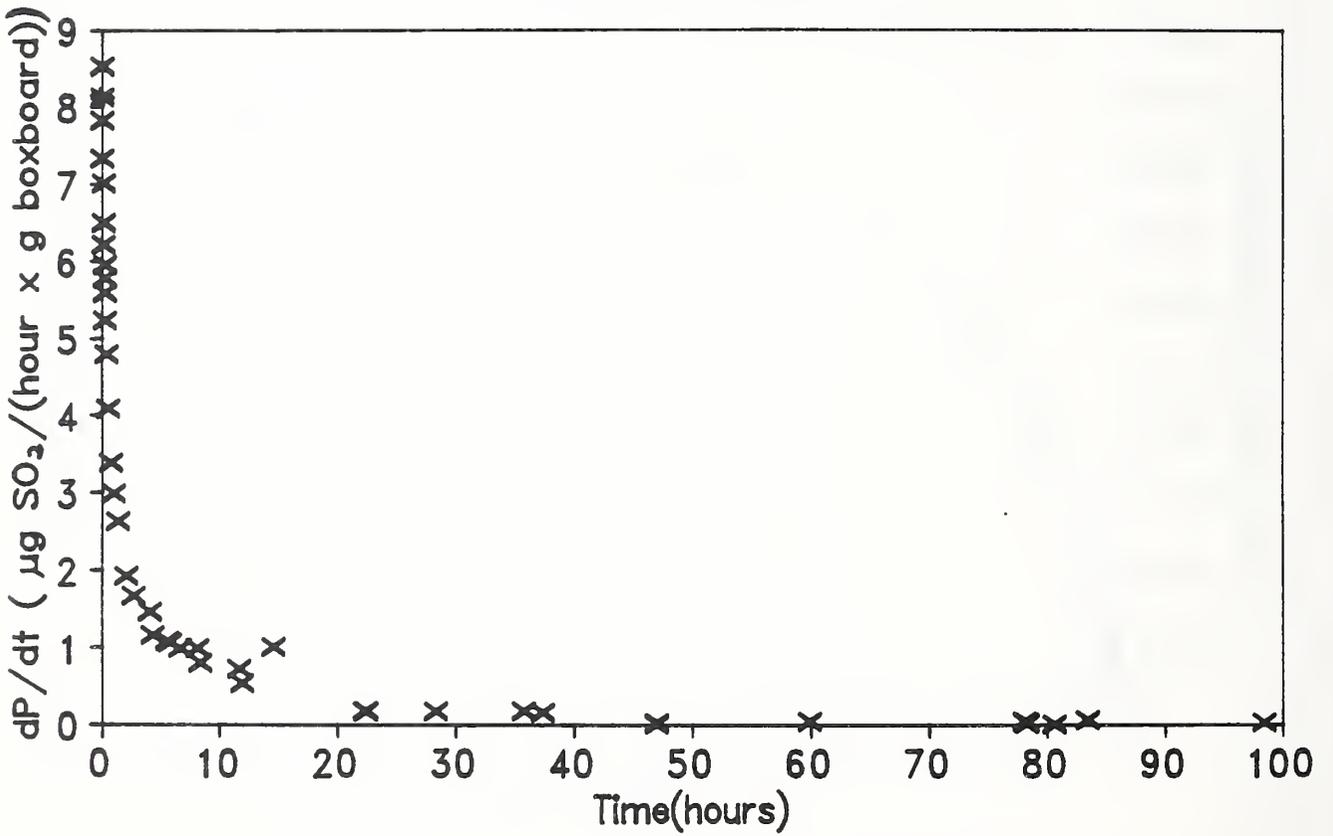


FIGURE 7

# ABSORPTION BOXBOARD A

Gas 147 ppm

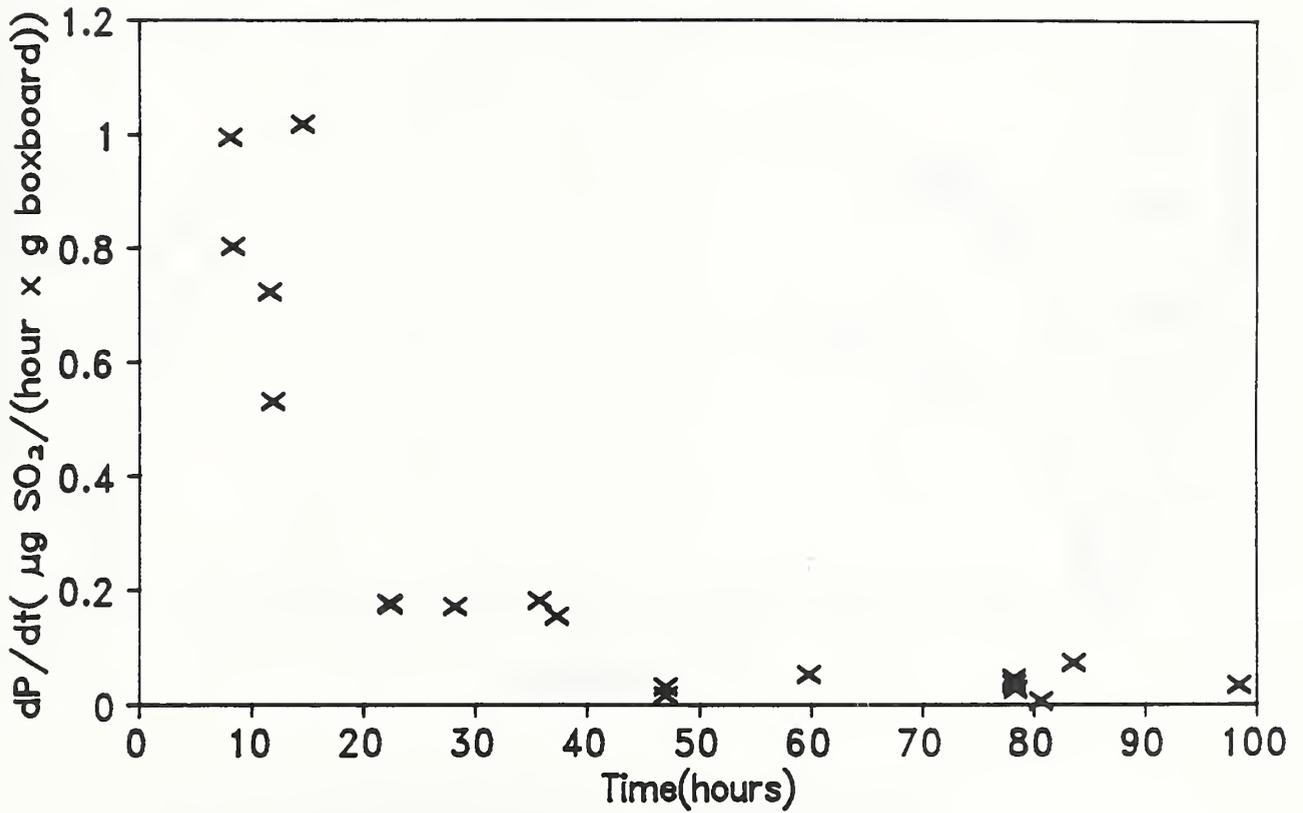
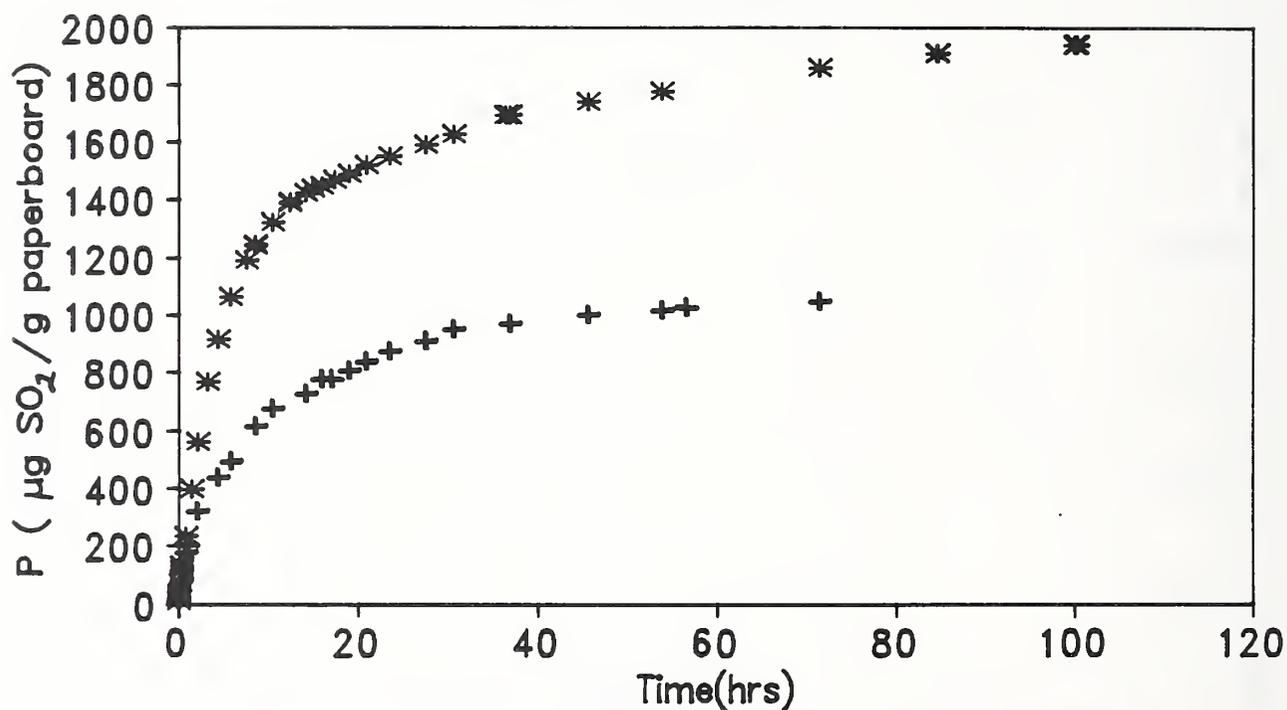


FIGURE 8

# ABSORPTION IN BOXBOARD A

Reabsorption after aeration

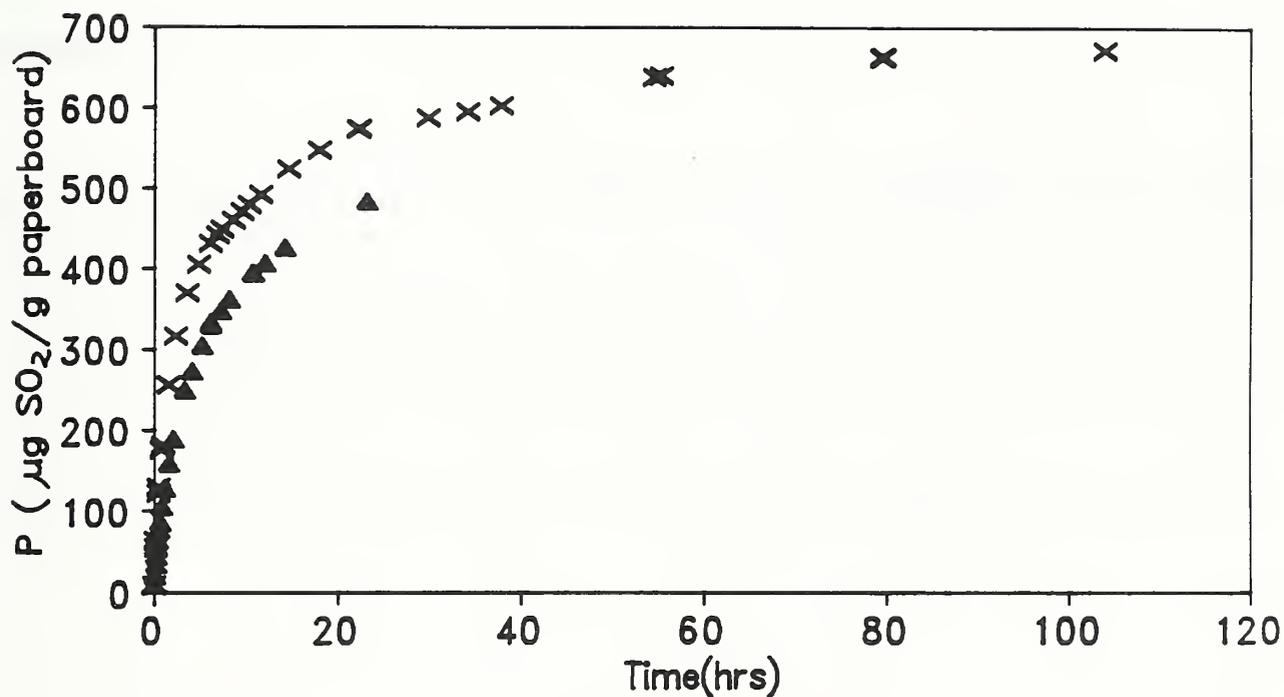


\* As received + Reabsorption

FIGURE 9

# ABSORPTION IN BOXBOARD B

Reabsorption after aeration at 60 ppm



× As received sample    ▲ Reabsorption



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The diffusion and absorption properties of boxboards, commonly used to store archival documents, with sulfur dioxide have been measured.

For the most common boxes used by National Archives and Record Administration a diffusion constant of about 0.001 cm<sup>2</sup>/sec is measured independent of gas concentration. These results are discussed in terms of Passaglia's model of the microenvironment provided by these boxboards as used in archival storage.

Uptake of sulfur dioxide by boxboard was found to be very dependent upon the nature of the boxboard sample. Both permanent and nonpermanent binding of SO<sub>2</sub> were observed and the contribution of each to the absorption of storage containers is discussed.

12. KEY WORDS (6 TO 12 ENTRIES; ALPHABETICAL ORDER; CAPITALIZE ONLY PROPER NAMES; AND SEPARATE KEY WORDS BY SEMICOLONS)

absorption, archival storage, boxboard, diffusion, diffusion constant, pollutants, sulfur dioxide

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