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Protection of Archival Records from Pollutants IV

**Absorption Studies of Archival
Box Boards and Model Papers
Exposed to $\mu\text{L/L}$ and nL/L
Concentrations of Nitrogen Dioxide**

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ABSTRACT

The absorption properties of archival storage containers (boxboards) exposed to $\mu\text{L/L}$ and Nl/L concentrations of nitrogen dioxide (NO_2) have been measured. Also measured were the absorption properties of several specially made paper samples containing various amounts of cellulose, kraft, lignin, and calcium carbonate (CaCO_3) components. The measurements were made on an apparatus that directly determined NO_2 absorbed from a flowing gas stream. The data showed NO_2 absorption by the samples to be dependent on the initial concentration of the NO_2 . The NO_2 absorption was greater for sample papers with higher amounts of kraft. Samples with 3% CaCO_3 absorbed more NO_2 than samples with no CaCO_3 . However, the samples with 3% CaCO_3 and those with 6% CaCO_3 absorbed the same amount of NO_2 .

FOREWORD FROM NARA

This report is the fourth in a series on research to investigate microenvironment effects on the storage of archival records, carried out by the National Institute of Standards and Technology for the National Archives & Records Administration (NARA). The genesis of this work was the initial report, "The Characterization of Microenvironment and the Degradation of Archival Records: A Research Program" by Elio Passaglia. Passaglia's report suggested that the protection NARA boxes afford their contents to common air pollutants could be judged by measuring the diffusion and absorption properties of these boxes with respect to common indoor air pollutants. Among various samples described in the current report, the absorption properties of two boxboards used at NARA were studied. The two boxboards studied are not the only boxboards in use at NARA, and should not be construed as 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).

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1.0 INTRODUCTION

The preservation and storage of materials are major concerns to archivists.^{1,2} Important information stored on many media, including papers, polymeric films, and paintings is lost through degradation. Each medium suffers from its own particular susceptibility to attack from external environmental parameters and auto-degradation mechanisms.

Through a research grant from NARA we previously studied various aspects of the preservation and storage of cellulosic materials. Our first report (Part I of this series), summarized studies describing the degradation products from rag paper and newsprint stored under low temperature (60 °C) accelerated aging conditions.³ Results of these studies showed that the composition of degradation products of paper is dependent on the microenvironment that surround the paper. This led to the question of the role of boxboard storage containers in mediating degradation processes. Is the boxboard container merely a passive element, does it actively participate in the degradation of the stored documents, or does it impart some level of protection to the materials that it contains?

The second report in this series (Part II) described the diffusion and absorption properties of two NARA boxboards in the presence of $\mu\text{L/L}$ (parts per million) concentrations of sulfur dioxide.^{4,5} The sulfur dioxide diffusion constant for the two NARA boxboards studied was about $1 \times 10^{-3} \text{ cm}^2/\text{s}$. Using SO_2 measurement techniques available to us at the time, the absorption of SO_2 at 10 $\mu\text{L/L}$ to 100 $\mu\text{L/L}$ was measured on both the NARA boxboards. It was found at the higher concentrations that the rate of absorption of SO_2 dropped to zero at long times, suggesting that the sites available for SO_2 absorption had saturated. Under these conditions we could study the difference between permanent and nonpermanent binding. The two samples showed very different effects of binding.

The third report in this series (Part III) described the diffusion and absorption properties of various boxboards in the presence of $\mu\text{L/L}$ concentrations of nitric oxide.⁶ In that study the absorption of nitric oxide (NO) was unmeasurable at concentrations of 10 $\mu\text{L/L}$ of NO in the reference gas. We estimated that less than 0.3 μg of NO per gram of paper was absorbed at this concentration. This compares to nearly 700 μg of SO_2 per gram of paper absorbed at this concentration as reported in the second study and the more than 300 μg of nitrogen dioxide (NO_2) absorbed per gram of boxboard found in the current study.

This report is Part IV in the series of research efforts that address issues about the preservation of archival materials. Herein, measurements of the absorption of nitrogen dioxide (NO_2), a major component of air pollution, by various boxboard materials are summarized. We will also provide NO_2 absorption data on various specially made paper samples incorporating varying proportions of cellulose, kraft, lignin, and calcium carbonate (CaCO_3), the components used in making boxboard materials.

Some the earlier studies have examined the effect of NO_2 on the properties of papers. Passaglia noted that although it is known that NO_2 attacks cellulose, few studies had been made on the absorption properties of NO_2 by paper at the time of his review.² He quotes a single study on cotton in which the degradation of cotton was studied. Studies on the effect of NO_2 on the strength of paper have been reported by Iverson and Kolar⁷. Leary and Zou⁸ investigated the effect of NO_2 on light absorption of papers.

The largest group of studies of the absorption of a pollutant gas by paper is that of Hudson and his collaborators on SO_2 .⁹ These researchers used a radiotracer technique to determine the amount of SO_2 absorbed by the sample of paper. However, radiotracer techniques are not available for systems involving NO_2 .

Williams and Grosjean¹⁰ studied the absorption of papers, both deacidified and normal, by the pollutants SO_2 and NO_2 using chemical means and by monitoring gas loss from the stream; the latter method is similar to ours. They examined newsprint and white woven papers. In the chemical method, they looked for the presence of nitrate and nitrite ions extracted from the paper after the paper had reacted with the pollutant gas. In the NO_2 experiments they found, to within a relatively large error, more moles of NO_2 in the form of NO_2 reacted to give nitrate and nitrite in the paper than they measured as NO_2 lost from the gas stream. Recently, Gurnagul and Zou¹¹ have reviewed much of the earlier work on the effects of SO_2 and NO_2 on paper permanence.

In the apparatus described in this paper, the depletion of the pollutant in the gas phase due to absorption of various paper samples is measured, as described below in Section 2.2.1. Techniques like the radiotracer method of Hudson and collaborators and the chemical analysis method of Williams and Grosjean that measure the amount of gas reacted with the paper sample, are not particularly appropriate for determinations of the amount of gas taken out of the air by the protective box material. Both techniques measure the amount of gas that is resident in the sample. The radiotracer method of Hudson and collaborators has the advantage over the Williams and Grosjean chemical method in that the radiotracer method measures actual

sulfur dioxide absorbed while the Williams and Grosjean technique requires that the form of nitrogen in the paper be known. One has to also assume that the form of the pollutant is unaffected on extraction with water. Furthermore, both the radiotracer technique and the chemical technique suffer from the possibility of gas loss during the transfer from the absorption chamber to the measuring chamber. In fact, in the method used by Hudson and his collaborators, the pollutant gases are blown off the paper before the measurement is made.

Our study differs from previous studies in that we employ computerized, automatic data collection to monitor pollution gas absorption continuously during the experiment systematically. Our experimental design directly addresses the question of the protective properties of the archival boxes (boxboard) by measuring the loss of pollutant gas from an air stream passed around the boxboard sample. By determining this parameter, one can hope to make predictions of the protective properties of the various boxboard types.

Finally, we measure the NO₂ absorption of a variety of specially formulated paper samples with known compositions. The purpose is to determine which formulation for boxboard is most protective for the storage box contents.

2.0 ABSORPTION OF NITROGEN DIOXIDE BY ARCHIVAL BOXBOARD AND MODEL PAPERS

2.1 Experimental

2.1.1 Chemicals and Materials.

Cylinders of 2 μL/L to 100 μL/L concentrations of nitrogen oxide (NO) in nitrogen (N₂) and nitrogen dioxide (NO₂) in air were obtained from Scott Specialty Gases (Plumsteadville, PA)¹² and used as received. Permeation tubes of NO₂ were obtained from VICI Metronics Inc. (Santa Clara, CA). Both tubular and wafer permeation devices were used in the studies described below.

Record storage boxes, used in normal NARA operations, were obtained from NARA. Boxboard samples for use in the absorption apparatus were cut from the lids and sides of these boxes. Samples designated as NARA A were cut from a gray box with white backing marked acid free. Samples designated as NARA B were cut from a beige box marked low lignin.

Papers with varying, known concentrations of cellulose, kraft and CaCO₃ were prepared for us by Conservation Resources International Inc. (Springfield, VA). Unbleached kraft was used to obtain some appraisal of the effect of lignin. The sample designated CR1 was a paper of pure alpha cellulose without lignin

or CaCO_3 . This material was prepared with about 3% and 6% CaCO_3 by mass to allow investigation of the effect of the CaCO_3 buffer in the pure cellulosic paper. These variations are designated as samples CR2 and CR3, respectively. A mixture of 50% alpha cellulose and 50% unbleached kraft by mass and no CaCO_3 was designated paper sample CR4. Sample CR5 was composed of 100% unbleached kraft and no CaCO_3 . Sample CR6 was a mixture of 50% alpha cellulose and 50% unbleached kraft, with 3% CaCO_3 all by mass. Sample CR7 was 100% unbleached kraft and 3% CaCO_3 by mass. The above descriptions of the specially prepared paper samples are summarized in Table 1.

Analyses of the amount of CaCO_3 in many of the samples were performed by Galbraith Laboratories, Inc. (Knoxville, TN). The percent CaCO_3 by weight as Ca and the percent by weight as CO_3 in each sample were both determined and are given in Table 1. If the calcium carbonate data were reported as $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$, the percentages would be twice the values reported in Table 1. Thus, we assume the amount of CaCO_3 added to the papers during their preparation to agree with the amount Galbraith Laboratories found, except sample CR7, which has much less CaCO_3 than was originally specified.

2.1.2 Presence of HNO_3

As noted above, both compressed gas cylinders and permeation tubes were used as NO_2 sources in this work. The cylinders of known NO_x concentration were mainly used to calibrate the NO_x detector. This was necessary because cylinders of NO_2 in air have been found to contain from 2 to 20 mole percent HNO_3 in them.¹³ Since we would expect HNO_3 to react very differently than NO_2 with paper, we wished to design experiments which exclude any HNO_3 from our absorption apparatus.

We also designed our experiments to avoid producing HNO_3 in the flowing gas stream that bathed the paper samples. This was done by flowing dry air over the NO_2 permeation tubes and down stream of the permeation tubes, mixing the NO_2 containing gas stream with a stream of humidified air, devoid of any water droplets (NO_2 forms HNO_3 in water droplets). Humid air without droplets was obtained by flowing dry air through an 8 foot long by 3 inch diameter horizontal poly(vinyl chloride) pipe in which 0.8 to 1.5 L of saturated salt solution was contained. To increase the saturated salt surface area, the inner circumference of the tube was lined with Whatman (Whatman Lab Sales, Hillsboro, OR) number 1 filter paper, obtained in 46 by 57 centimeter sheets. Air entering the tube was not bubbled through the saturated salt solution but only flowed over it.¹⁴ Under these conditions, the humidity tube can produce a continuous stream of humid air flowing at up to 500 cm^3/min at the saturated salt solution relative humidity for weeks at a time.

Using the above humidity generating apparatus and NO₂ permeation tubes, Robert Sams of the Organic Analytical Research Division, NIST, used a long path gas cell in a vacuum IR instrument to look for HNO₃ in our NO₂ stream at an NO₂ volume fraction of 50 μL/L and a relative humidity of 42%. No HNO₃ was found to within the sensitivity of the experiment. Appendix A contains a description of the IR experiment and the results obtained.

2.1.3 Apparatus

Absorption measurements were performed using the apparatus shown in figure 1. Air flowing at a fixed rate was passed through a glass U-tube containing one or more NO₂ permeation tubes. The glass U-tube was immersed in a water bath at a fixed temperature, typically between 5 and 30 °C. The air exiting the U-tube, with a fixed concentration of NO₂, was now mixed with a stream of humid air. The gas mixing vessel was constructed from a 250 mL Pyrex round bottom flask, filled approximately half full with Pyrex glass beads 6 mm in diameter. The inside surface of the mixing vessel and the glass beads inside it were surface treated with 1,1,1,3,3,3-hexamethyldisilazane (Aldrich, Milwaukee, WI) to reduce absorption of NO or NO₂ onto the surface of the glass. Flow rates and relative humidities of mixing air were adjusted to produce the desired relative humidities and NO₂ concentrations. The air stream, with an NO₂ concentration of C_{in}, was passed into the sample absorption chamber. As the mixture of humid air and NO₂ gas passed the boxboard sample, the NO₂ gas was absorbed and its concentration decreased. The diminished concentration at the outlet side was measured. In the measurements report below, the flowing gas stream relative humidity was 44 ± 2% and sample absorption chamber temperature was 26 ± 2°C except when otherwise noted. In a few experiments we have raised the humidity to see the effect of different humidity levels on our measurements.

Nitrogen dioxide concentrations were measured using a Model 14A, NO/NO₂/NO_x chemiluminescent analyzer (Thermo Environmental Instruments Inc., Franklin, MA). This instrument was calibrated using N₂ gas mixed with NO or air mixed with NO₂ at 0.20 μL/L or 100 μL/L from commercially supplied cylinders described in section 2.1.1. At least five different concentrations were measured for each of the three instrument concentration range settings used during absorption measurements. Calibrations were done with the instrument operated in the NO_x mode. The calibration gas concentration was adjusted by mixing the NO₂ and N₂ gasses at different flow rates. Materials in the experimental apparatus in contact with NO and NO₂ were 316 stainless steel, Pyrex glass, short lengths of tygon tubing, or

tubing made of the copolymer of tetrafluoroethylene-hexafluoropropylene.

During the calibration of the NO/NO₂/NO_x detector, it was found that NO transforms to other forms of NO_x in the presence of oxygen and laboratory fluorescent light. No such problems were found with NO₂. However, as a precaution, all experiments were carried out in the dark.

Sierra Instruments, Inc. (Monterey, CA) Models 840 and 860 and Tylan General (San Diego, CA) Model FC-280AV flow controllers were used to regulate gas flow rates in these absorption experiments. All controllers were calibrated using soap film flow meters and a stopwatch. Six data points at four flow rates were taken for each controller. Flows were regularly checked, usually at the end of each absorption measurement experiment, to confirm that the gas flows were being controlled at the expected rates. The flow controllers were found stable enough that inaccurate flow rates were rarely discovered.

Since the experiments were of multiple days duration, the data collection and control of the gas flow paths during the experiment were automated using an IBM (Armonk, NY) AT computer with an AP200 controller card from Strawberry Tree, Inc. (Sunnyvale, CA). The computer program controlled the frequency at which the detector voltage was read and stored. The program also controlled a system of Whitey (Whitey Co., Highland Heights, OH) 4-way pneumatic valves which modified the gas flow path of the apparatus. In a typical experiment, the active NO₂ pollutant gas bypassed the absorption chamber for about 1200 s while its concentration was measured and a C_{ref} value obtained. This C_{ref} gas concentration value is referred to in the following text as the reference concentration. After the C_{ref} concentration was measured, the gas stream was switched to flow through the absorption chamber during which time C_{out} was measured every 300 s to 1200 s. The system was stable enough so that we did not need to measure the reference concentration more than once every 6 h to 10 h. Thus, the NO₂ pollutant gas flowed through the absorption chamber for a time period that was 18 to 30 times longer than the length of the reference gas measurement interval, when the NO₂ pollutant gas was bypassing the absorption chamber. The small amount of time that the NO₂ gas flow was diverted from the absorption chamber was considered unimportant in determining the total NO₂ pickup.

During some early experiments we tried to have a second gas stream, with NO₂ concentration and humidity matched to that of the reference gas, flowing through the absorption chamber during the time period when the main pollutant gas stream was bypassing the absorption chamber. We found the permeation tubes so inconsistent in output of NO₂ that we could never get a good

concentration match for the length of the experiment (about 1 week). Thus, experiments were run with no gas flowing through the absorption chamber during the measurement of reference concentration.

2.2 Considerations on the Design of Experiments to Determine the Pickup of NO₂ by Boxboard.

To obtain a proper estimate of absorption of NO₂ by boxboard, the NO₂ absorption as a function of time and concentration must be examined. These data may provide information on the mechanism of NO₂ absorption by boxboard.

2.2.1 Analytical Considerations in the Design of the Flow-by Absorption Apparatus.

Nitrogen dioxide at volume fractions of microlitres of NO₂ per liter of air ($\mu\text{L/L}$) in humidified air was sent through the absorption apparatus (figure 1) of volume, V_c . The apparatus contains a boxboard sample of volume, V_p , and mass, m_p . Gas flows at a specific rate, q . The sample absorbs NO₂, thereby decreasing the NO₂ concentration in the gas. The concentration of the NO₂ at the inlet is C_{in} and that at the outlet is C_{out} . Both are expressed in units of grams of NO₂ per cubic centimeter of air. The mass flow equation that describes this condition is:

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

where J_{in} is the mass flow in g/s of pollutant flowing into the apparatus, J_{ab} is mass flow of pollutant absorbed, and J_{out} is the mass flow of pollutant exiting the apparatus. Furthermore,

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

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

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

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

where $P(t)$ is the concentration of pollutant absorbed by all mechanisms in the paper at time, t , in grams of pollutant per gram of paper. Therefore, the rate of NO₂ absorption into boxboard by any mechanism, dP/dt , is shown in equations 3.5 and 3.6.

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

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

Using the method described above permitted reliable measurements of total absorption of NO₂ to be made.

2.2.2 Use of dP/dt data.

The value for P may be obtained by integration of dP/dt using the following expression:

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

Most of the data in this report is presented in the format of P(t), the total absorption of pollutant per gram of paper after time, t.

2.3 Mass Pickup Data for NO₂ Absorption by NARA Boxboard and Various Other Papers

2.3.1 Estimation of the error in the overall experiment

In figure 2 we show repeated measurement of P, the mass of NO₂ absorbed per gram of sample, at about 7 μL/L NO₂ in air for three pieces of NARA A board. The samples, cut fresh from an NARA box, are not marked in the figure. At 100 hours the separation between the largest and smallest of the three is 20 μg of NO₂/g of sample. At 100 hours, the root means square standard deviation (rmsσ) of these is 10 μg NO₂/g of sample while at 50 hours it is 5 μg NO₂/g of sample. We have conducted repeated measurements on other samples. figure 3 shows NARA A board at 2.0 μL/L NO₂ and figure 4 and 5 show the same for NARA B board at 2.0 μL/L and 8.0 μL/L NO₂.

Considering the very limited quantities of the specially prepared paper samples available and the approximately one week required to run an absorption experiment, making repeat measurements on all samples was impractical.

In Table 2 we present the root mean squared standard deviation from the repeatability at 60 and 100 hours of the samples discussed in Figs. 2 through 5. There seems to be no systematic variation in these errors which fall in the range of 3% to 6%. The average of these errors is about 4.5%. A Student T Test for the two and three degrees of freedom for each of these points at a .90 to .95 confidence interval would make the overall estimated error twice the average root means square standard deviation about 9%. The factor of two is consistent with NIST policy on reporting errors.¹⁵ The 9% error is therefore taken to be the estimated error in our measurements.

A variety of experimental parameters enter the determination of the overall error. We will consider only two of them. First, there is the sample-to-sample variation. This error is difficult to evaluate. We cannot use the same sample in two absorption measurements since the second measurement of the absorption may be influenced by the binding of some NO_2 during the first experiment. The binding is discussed in more detail in section 2.4.

Another possible cause of error is the gas lost while the sample is placed into the apparatus or taken out of the apparatus. We show an example of opening the absorption chamber, leaving it open 30 seconds, closing the absorption chamber and putting no sample into the chamber. The response of the system to this sequence is shown in figure 6. At $8 \mu\text{L/L}$, we find that less than $1 \mu\text{g}$ of NO_2 is lost and the system returns to a baseline in less than 10 minutes. This mass is small compared with the total NO_2 absorption found after 10 hours for any of the samples examined in this report. Our experiments run at least 60 hours. Thus, the effect of opening and closing the apparatus was inconsequential in the estimation of the value of P.

2.3.2 Concentration Dependence of the NO_2 Absorption of NARA Boxboards

Measurement of the NO_2 absorption of NARA A and B boxboards and some specially prepared papers were made at concentrations of $8 \mu\text{L/L}$, $2 \mu\text{L/L}$, and 300 nL/L . The mass absorption as a function of time is shown for the sample NARA A boxboard in figure 7 and for sample NARA B boxboard in figure 8. As expected, the higher the concentration of NO_2 gas, the greater the absorption of material. Furthermore, even after more than 150 hours of measurement at these concentrations, we see no saturation. That is, none of the samples reach a condition where they stop absorbing NO_2 gas.

This result is in contrast to our earlier data on SO_2 at higher concentrations, where we found saturation (or near saturation). Attempts to make measurements at higher NO_2 concentrations were limited by baseline and reference stability at those higher concentrations. To generate the higher NO_2 concentrations, we used tubular permeation devices which provided a much less stable flux as a function of time than the wafer devices we used at the lower concentrations.

Plots of P, the NO_2 absorption, as a function of reference concentration, in $\mu\text{L/L}$ are given in figure 9. The plots show a possible linear behavior for the NARA B at 60 hours. The same data plotted in figure 10 against $\sqrt{(\mu\text{L/L})}$ for the reference concentration is very linear for the NARA A data. With only three reference concentration measurements per sample, these

results are far from conclusive but the linearity seen for NARA A data is very suggestive. Since the main difference between NARA A and NARA B samples is that NARA A contains lignin and NARA B does not, this suggests that the concentration dependence of NO₂ absorption for lignin is different from that for cellulose and CaCO₃.

We also point out that the effect of lignin in NARA A is to increase the amount of NO₂ absorption. At 8 μL/L, the amount of NO₂ absorbed by NARA A is almost double that of NARA B, the sample without lignin. This effect will be discussed in a later section.

2.3.3 Effect of Varying Percentage of Kraft on NO₂ Absorption

The use of lignin free boxboard material is considered advantageous for archival storage. Generally, this is not due to the effect of the lignin on pollutant gases but rather to the concern that the lignin degradation products may catalyze the degradation of the archival materials stored in the boxboard.³

We have investigated the effect of lignin by having papers (Table 1) made containing alpha cellulose mixed with kraft. The lignin content of 100% kraft is approximately 16%.¹⁶ In figure 11, the effect of kraft content on NO₂ absorption at an NO₂ concentration of approximately 2 μL/L is shown while in figure 12 the effect of kraft content on NO₂ absorption at an NO₂ concentration of approximately 8 μL/L is shown. The changes in absorption as a function of percent kraft is very great, well beyond any experimental error. At both concentrations of NO₂, we see significant effect of the lignin on the pickup of NO₂. This is consistent with our work on NARA boxboards where we found that the lignin containing NARA A boxboard picked up much more NO₂ than the lignin free NARA B boxboard.

2.3.4 The Effect of Varying CaCO₃ on the alpha Cellulose Samples

Calcium Carbonate (CaCO₃) is added to archival materials and other papers to act as a buffering agent against acid catalyzed degradation of paper. Paper and paper materials most easily degrade in acidic environments. The addition of CaCO₃ helps insure that the acid components are neutralized. Many of the pollutants which are of concern to archivists can form acid components harmful to paper. Earlier studies on the effects of SO₂ and NO₂ on the mechanical properties of paper show this effect.¹¹ Thus, it is expected that papers with CaCO₃ added should absorb more NO₂ than papers containing only alpha cellulose. NARA A and B boxboard samples contain a mass fraction of 3% CaCO₃. To see if more CaCO₃ would be effective in

absorbing more NO₂, samples with a mass fraction of 6% CaCO₃ were made (paper CR3).

The effect of CaCO₃ on the pure alpha cellulose paper is shown in figure 13 at 2 μL/L and in figure 14 at 8 μL/L NO₂ concentrations. The qualitative features of the figure are the same. The addition of the first mass fraction of 3% CaCO₃ (paper CR2) is to change the absorption of NO₂, while the addition of mass fraction of 3% more CaCO₃ (paper CR3) has no effect. To check that this observation was not due to an error in paper sample preparation and that sample with a mass fraction of 6% CaCO₃ was actually put into paper sample CR3, we had Galbraith Laboratories determine the percent CaCO₃ in the paper samples. It was found that the amount of CaCO₃ in sample CR3 was approximately twice that found in CR2. See discussion in section 2.1.1. and Table 1 for details of the CaCO₃ analyses.

2.3.5 The Effect of Varying Percent Kraft with Fixed CaCO₃

We attempted to investigate the effect of varying Kraft with a fixed amount of CaCO₃. Although sample CR7 was prepared to contain a mass fractions of 3% CaCO₃, the analysis by Galbraith Laboratories, Inc. indicates that much less than mass fraction of 3% CaCO₃ was present. Even with the reduced CaCO₃, CR7 has a larger absorption of NO₂ than CR6. This suggests that the effect of the mass fraction of 3% CaCO₃ on the absorption of NO₂ from the data displayed in figure 15 at 2 μL/L and figure 16 at 8 μL/L NO₂ concentrations is much smaller than the effect of adding more kraft. The qualitative features of the figures are the same. Increasing the kraft content increases the absorption of NO₂.

2.4 Estimations of the Character of the Binding of NO₂ to Samples

In an earlier study on SO₂, we could make some conclusions about the character of the binding of SO₂ to the boxboard samples used in that study. In that study, we looked at the difference between permanently bound and temporarily bound SO₂. It was concluded that permanently bound SO₂ had reacted with the sample by a mechanism which was irreversible on the time scale of a few weeks.

We distinguished between the two types of binding in the following manner. The SO₂ absorption of a fresh piece of boxboard (a sample not exposed to any other than ambient atmospheric SO₂) was measured. This measurement was made until saturation was reached. (See discussion of saturation below). The sample was then taken from the absorption chamber and exposed to ambient indoor atmospheric SO₂ concentrations for times of days to weeks. During this time any non-permanently bound SO₂ was desorbed. Thus, when the absorption experiment was repeated, if the same amount of SO₂ was absorbed at saturation during the

second exposure, then all the SO₂ initially absorbed was desorbed while the sample was at ambient concentration. If less SO₂ was absorbed during the second exposure, then the difference between the two quantities was presumed to be the permanently bound material.

This study was conducted by having the SO₂ absorption continue until the boxboard was saturated or nearly saturated. Once the boxboard was saturated, no more SO₂ could be picked up and the samples were placed at ambient SO₂ concentration to allow unbound SO₂ to desorb. At the high concentrations of the SO₂ study, saturation occurred within a week, or so. Saturation was important because it showed the total amount of SO₂ which the sample could absorb, or the number of sites available in the sample for absorption. The difference in quantities of SO₂ absorbed between the first and second absorption experiments showed the number of sites which remained filled even after desorbing for a week or so, thus suggested that those sites were permanently filled.

At the NO₂ concentrations used in the current study, no saturation occurred even for exposure periods up to 2 weeks. Saturation is assumed when the absorption, P, is unchanged as a function of time. In the plots of NO₂ absorption, saturation is characterized by a P(t) curve parallel to the time axis as the experiment continued. None of our studies, even those at higher NO₂ concentrations, showed any signs of saturation.

Although measurements taken to saturation allow one to make quantitative estimates of the effects of permanent binding, one could see the effect of permanent and non-permanent binding in a nonsaturation study. To evaluate this effect, we used the following reasoning. Even the initial absorption can be affected by the total number of binding sites available. If an initial absorption changes the number of sites by making some of them unavailable due to permanent binding, then there may be some measurable change produced during the second absorption experiment. If there is a measurable change (larger than the expected error) on the second absorption after desorption, then we may argue that there is some effect on bound sites. If there is no observable effect, then we are unable to conclude the presence or absence of permanent binding sites. This is because in the NO₂ absorption experiments, either there may be no permanently bound NO₂ or there may be some permanent binding but its effect may be very small on the absorption during the time of our measurement.

Curves marked "C" and "rerun C" in figure 4 represent data from the same NARA B sample at 2μL/L reference. (They are both dashed lines in figure 4.) Curve C is the data from the first run. The NARA B sample was then taken out of the absorption

chamber and stored 3 weeks. After airing in the room over night, the sample was returned to the absorption chamber for a second time. Curve "rerun C" is the data from the second run. Curve C is always greater than curve "rerun C". At 70 hours, curve C is 1.5 $\mu\text{g NO}_2/\text{g}$ of sample greater than "rerun C". This suggests that some absorption sites are lost to the initial exposure to NO_2 and thus, there is an effect of permanent binding on the absorption. However, on the same plot we have a fresh sample which is more than 1.5 $\mu\text{g NO}_2/\text{g}$ of sample different from the other suggesting that the 1.5 $\mu\text{g NO}_2/\text{g}$ of sample at 70 hours is the noise in the experiment. This can be confirmed by noting at 70 hours the total absorption is 30 $\mu\text{g NO}_2/\text{g}$ of sample. With the expected 9% error discussed in section 2.3.1, we expect a sample to sample variation of 2.7 $\mu\text{g NO}_2/\text{g}$ of sample. Thus, what ever small binding is seen here is masked by the experimental error.

A similar discussion can be made for NARA A board. Curves marked "D" and "E" in figure 3 represent data from the same NARA A sample at 2 $\mu\text{L/L}$ reference. (They are both dashed lines in figure 3.) Curve D is the data from the first run. The NARA A sample was then taken out of the absorption chamber and stored 4 days. After airing in the room over night, the sample was returned to the absorption chamber for a second time. Curve "E" is the data from the second run. Curve D is always greater than curve "E". At 70 hours, curve D is 7.6 $\mu\text{g NO}_2/\text{g}$ of sample greater than curve "E". At 100 hours this difference is 10 $\mu\text{g NO}_2/\text{g}$ of sample. This again suggests that some absorption sites are lost to the initial exposure to NO_2 and thus, there is an effect of permanent binding on the absorption. However, on the same plot we have a fresh sample which is more than 20 $\mu\text{g NO}_2/\text{g}$ of sample different from the other samples after 100 hours suggesting that the 10 $\mu\text{g NO}_2/\text{g}$ of sample at 100 hours may be the noise in the experiment. This can be confirmed by noting at 100 hours the total absorption is about 160 $\mu\text{g NO}_2/\text{g}$ sample. With the expected 9% error discussed in section 2.3.1, we expect a sample to sample variation of 14.4 $\mu\text{g NO}_2/\text{g}$ of sample. Thus, what ever small binding is seen here is masked by the experimental error.

3.0 CONCLUSIONS

The absorption characteristics of various components of boxboards used in the construction of archival storage boxes has been studied. Of all the components, lignin (or kraft) has by far the largest influence on the absorption of NO_2 by boxboard materials. The buffering material, CaCO_3 , also enhances NO_2 absorption, although not to the extent that kraft does. Increasing the CaCO_3 content in the sample papers above 3% does not seem to increase the NO_2 absorption. The reason for this is unclear at this point. Further study is suggested.

At 60 h, 50% kraft with 8% lignin had absorbed three times the NO_2 as pure alpha cellulose alone, while the 100% kraft had absorbed nearly 5 times more NO_2 . Thus, lignin, by imparting a greater NO_2 absorption capacity to papers, is better protection against NO_2 than CaCO_3 .

Earlier studies on SO_2 at higher concentrations than those considered here on NO_2 are consistent with this finding. Further, our studies on NARA boxboards with and without lignin but both having 3% CaCO_3 show the same behavior with NO_2 .

Our inability to attain saturation for NO_2 absorption preclude attempts to estimate the lifetime of a particular boxboard for absorption of NO_2 . For example, if the boxboard had a saturation point of $1000 \mu\text{g NO}_2/\text{g}$ of boxboard (a level close to that for SO_2 found earlier) and if dP/dt is $0.001 \mu\text{g NO}_2/\text{hour}$ at 75 nL/L in air, then we may expect that the boxboard will absorb NO_2 at the measured rate of dP/dt for about 10^6 hours or approximately 10 years.

4.0 ACKNOWLEDGMENTS

The support for this project came from a grant from NARA. The authors would also like to thank W. Hollinger of Conservation Resources International, Inc. for providing paper samples and discussions on the boxboards and manufacturing process. The authors also appreciate the data analysis work of our volunteer summer student Frank Yang (Lancaster High School, Lancaster, PA).

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 13. Private communication Bill Dorko, Bill Thorn and Robert Sams, Organic Analytical Research Division, NIST.
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TABLE 1

Sample ID	Description of Sample ² all % as mass fractions	% mass fraction CaCO ₃	
		from CO ₃	from Ca
NARA A	60 pt, composite, acid-free, 3% CaCO ₃ reserve, cut from NARA box		
NARA B	60 pt, composite, low-lignin, 3% CaCO ₃ reserve pH 8.5, cut from NARA box		
CR 1	100% alpha cellulose sheet, no lignin, no CaCO ₃	<.04	0.1
CR 2	100% alpha cellulose sheet, no lignin, 3% CaCO ₃	1.8	2.0
CR 3	100% alpha cellulose sheet, no lignin, 6% CaCO ₃	3.3	3.4
CR 4	50% alpha cellulose, 50% unbleached kraft, no CaCO ₃		
CR 5	100% unbleached kraft, no CaCO ₃	<.04	0.4
CR 6	50% alpha cellulose, 50% unbleached kraft, 3% CaCO ₃	1.2	2.6
CR 7	100% unbleached kraft, 3% CaCO ₃	0.7	1.2

TABLE 2

The standard deviation in P , $\sigma(P)$,
divided by the absorption, P
as a percent

Sample	Concentration reference, $\mu\text{L/L}$	$\sigma(P)/P$ at 60 hours	$\sigma(P)/P$ at 100 hours
NARA A	8.0	4.6%	2.8%
	2.0	5.3%	3.8%
NARA B	8.0	4.2%	3.9%*
	2.0	6.3%	

Average standard deviation of P as a percent of P is 4.5%

* data taken at 90 hours

APPENDIX A

U.S. DEPARTMENT OF COMMERCE

NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY

GAITHERSBURG, MD 20899

May 6, 1994

REPORT OF ANALYSIS

TO: Charles Guttman
Polymers Division
Materials Science and Engineering Laboratory

From: Robert L. Sams
Gas Metrology Research Group
Organic Analytical Research Division
Chemical Science Technology Laboratory

Subject: Determination of HNO_3 concentrations in low (about
13 $\mu\text{L/L}$) concentration of NO_2 using FTIR detection.

Method: A vacuum Bruker FTIR model 66V was used in conjunction with a 5.28 m path to determine the concentration of nitric acid in an NO_2 in breathing air mixture with relative humidity up to 40%. The NO_2 concentration was determined using the 2900 cm^{-1} ($\nu_1 + \nu_3$) band. The spectrometer was run at a resolution of 0.8 cm^{-1} and 500 co-adds to increase signal to noise. The absorbance was referenced to a $443\text{ }\mu\text{L/L}$ standard taken in a 20.69 cm cell.

Sample Introduction: The sample was flowed through 5.28 m path length white type cell and the pressure was measured by a MKS baratron to be 748.6 torr.

Measurement Technique: First dry breathing air flowing at about 100 cc/min was measured, then dry breathing air with about 13 $\mu\text{L/L}$ was introduced into the cell and measured at the same flow rate. The next set of measurements were made on moist (about 40% relative humidity) NO_2 in breathing air at about 13 $\mu\text{L/L}$ NO_2 . The humid air was flowed through the cell over night at 100 cc/min in order to come to equilibrium. The last set of measurements were when the flow rate was lowered at about 20 cc/min and flowed through the cell over night. However, the flow never got completely through the white cell because of too much back pressure.

Results: The $\nu_1 + \nu_3$ band of NO_2 had to be used in the data reduction phase because of overlapping of water in the 1600 cm^{-1} region. Integrated band intensities could not be used because of overlapping problems so a relative peak height technique was used. The nitric acid was estimated from a 879 cm^{-1} Q branch and the $65 \text{ }\mu\text{L/L}$ reference spectrum taken in the 20.69 cm cell. The concentration of nitrogen dioxide in the dry NO_2 was $11 \text{ }\mu\text{L/L}$ with a lower bound of 25 nL/L for HNO_3 . In the 40% relative humidity breathing air the total NO_x was calculated to be $12.3 \text{ }\mu\text{L/L}$ with $11 \text{ }\mu\text{L/L}$ NO_2 and $1.3 \text{ }\mu\text{L/L}$ HONO both cis and trans and the estimated concentration of HNO_3 was less than 35 nL/L . In the last set of measurements on the low flow the concentration of NO_2 was about $25 \text{ }\mu\text{L/L}$ with about $6 \text{ }\mu\text{L/L}$ HONO. Since this last set of measurements never came to equilibrium because of its low flow rate these numbers are probably a little below the input concentration of NO_2 .

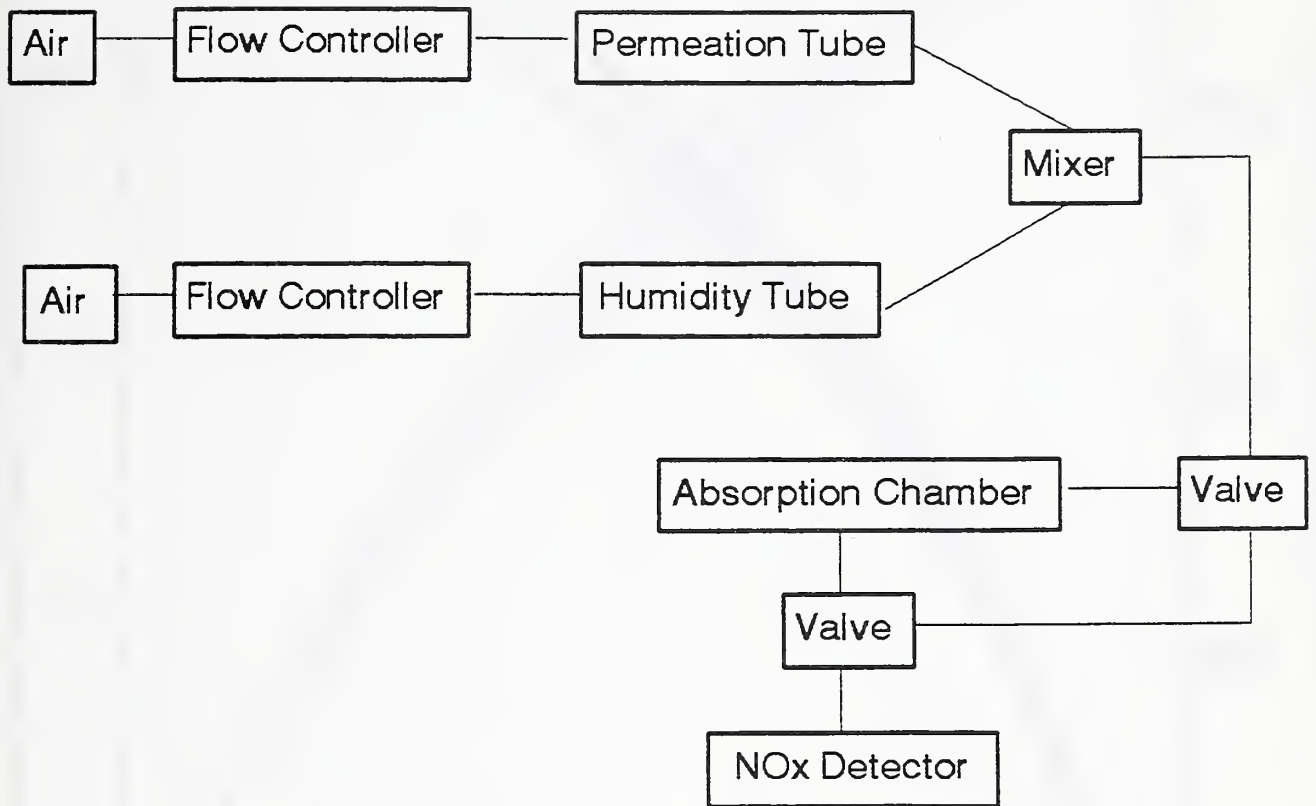


Fig 1. Schematic of NO₂ absorption apparatus.

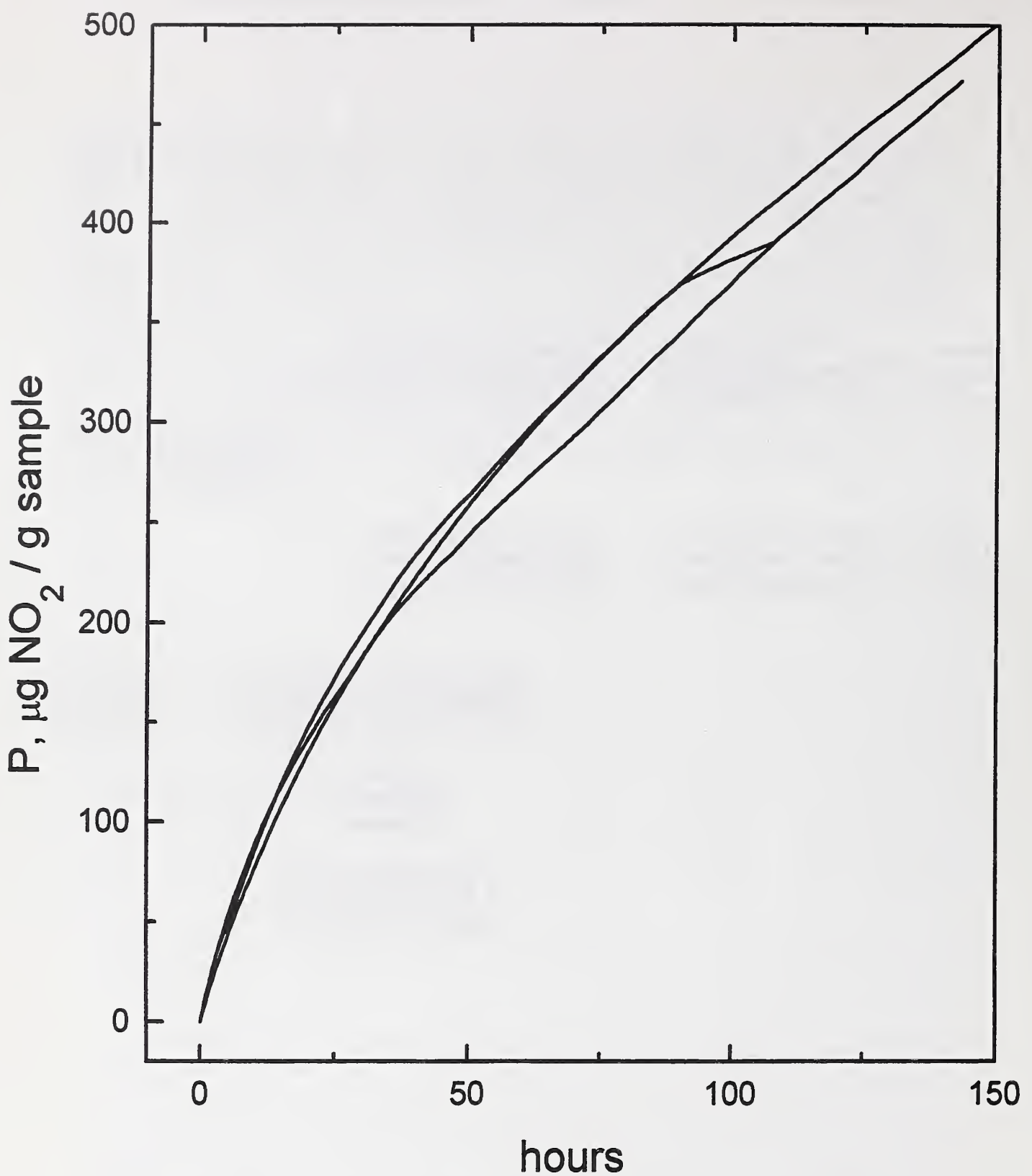


Fig 2. Repeats of 3 NARA A boards at about 8 $\mu\text{L/L}$. The closeness of the NO_2 absorption per gram, P, indicates the repeatability of the absorption experiment.

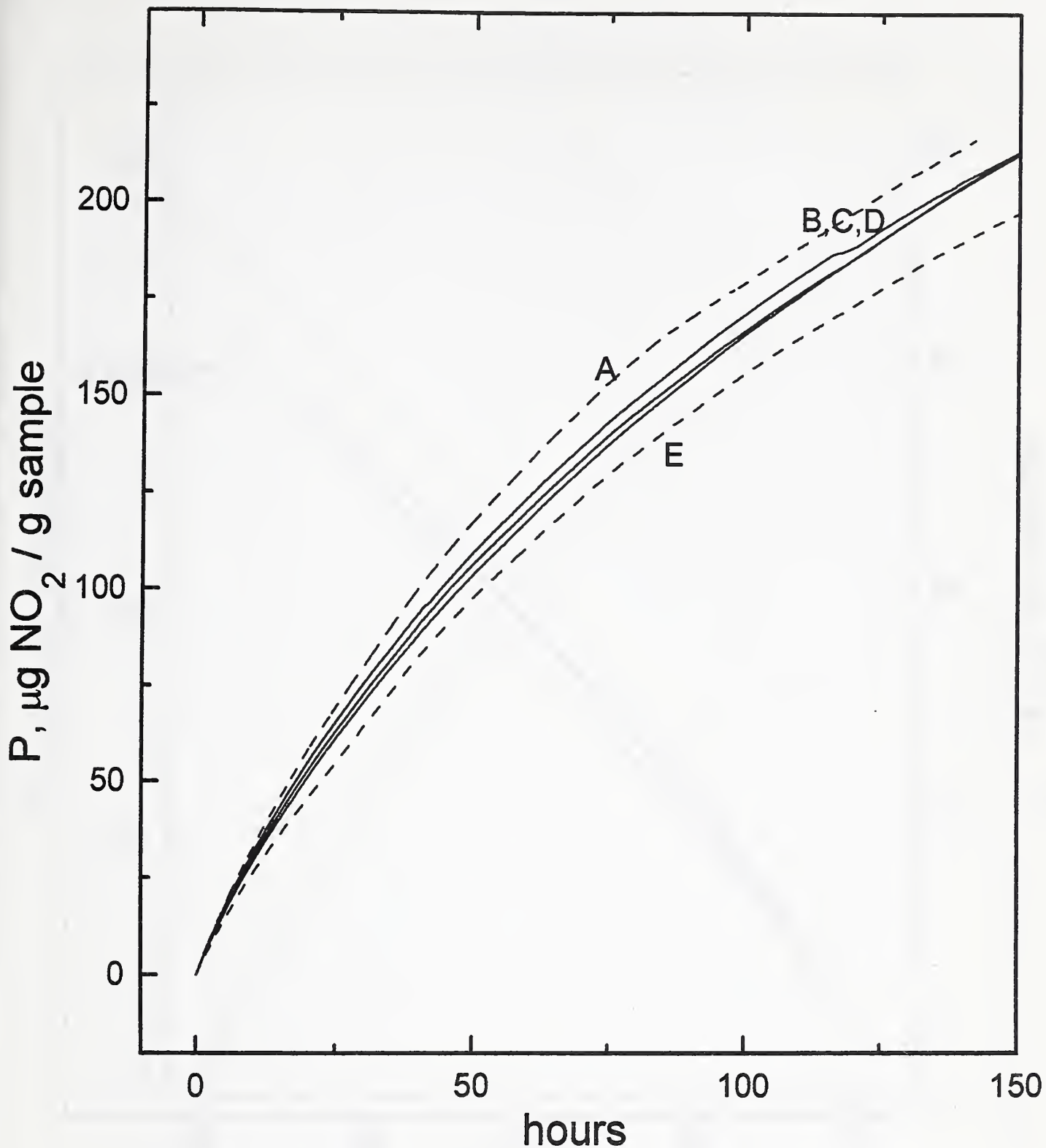


Fig 3. Five experiments on NARA A boxboards at 2 $\mu\text{L/L}$ reference. The closeness of the pickup, P, per gram of boxboard shows the repeatability of the absorption technique. Curve marked A-D are boxboards of different weights and thus indicate the repeatability of the experiment. Curve D is not a fresh board cut from a box but is a run of boxboard B after it aired for a

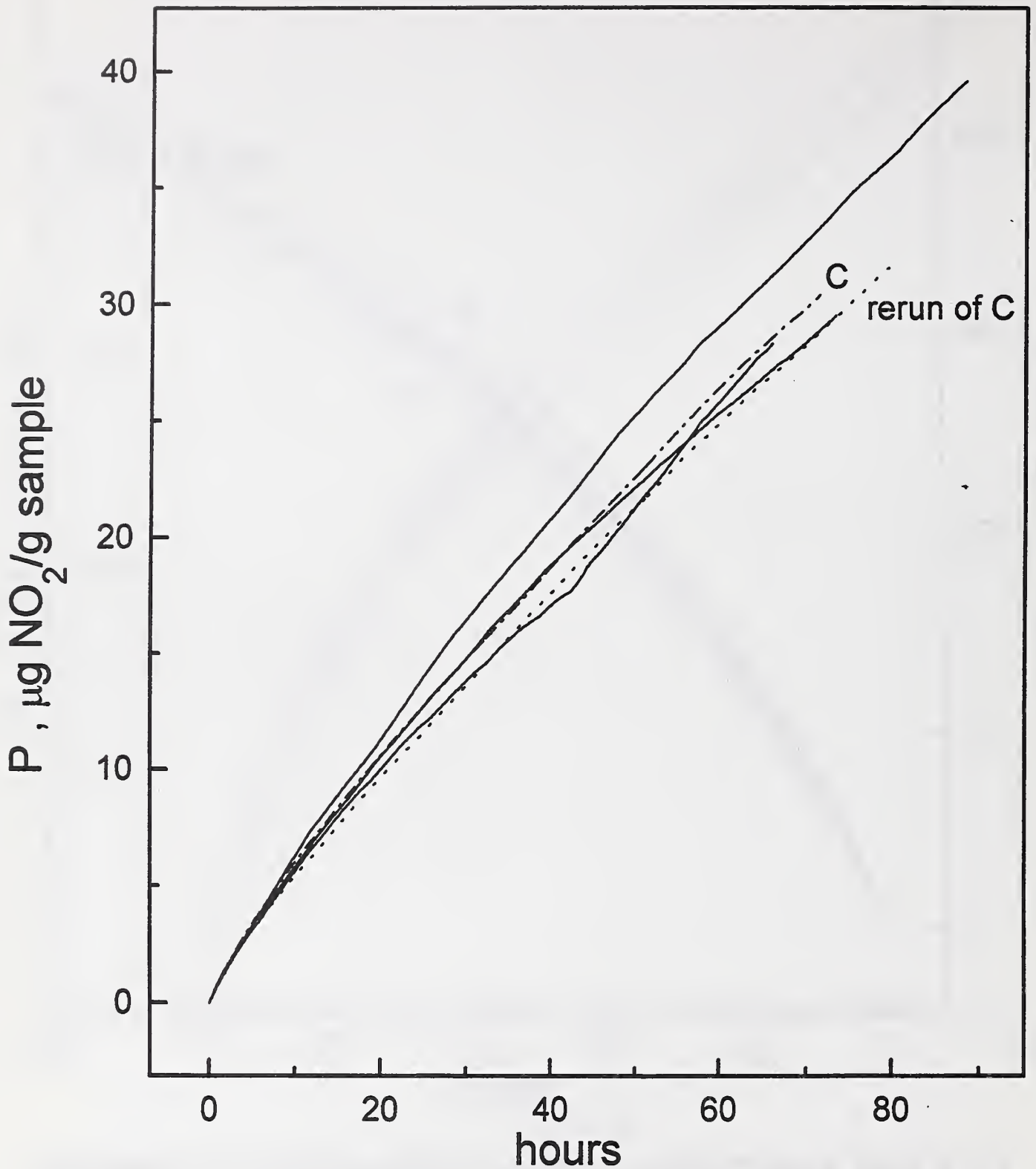


Fig 4. Repeats of board NARA B at about 2 $\mu\text{L/L}$ reference. This shows the repeatability of the experiment. The lower of the dashed curves marked rerun of C is data from a reabsorption experiment on the same used to get data in curve marked C

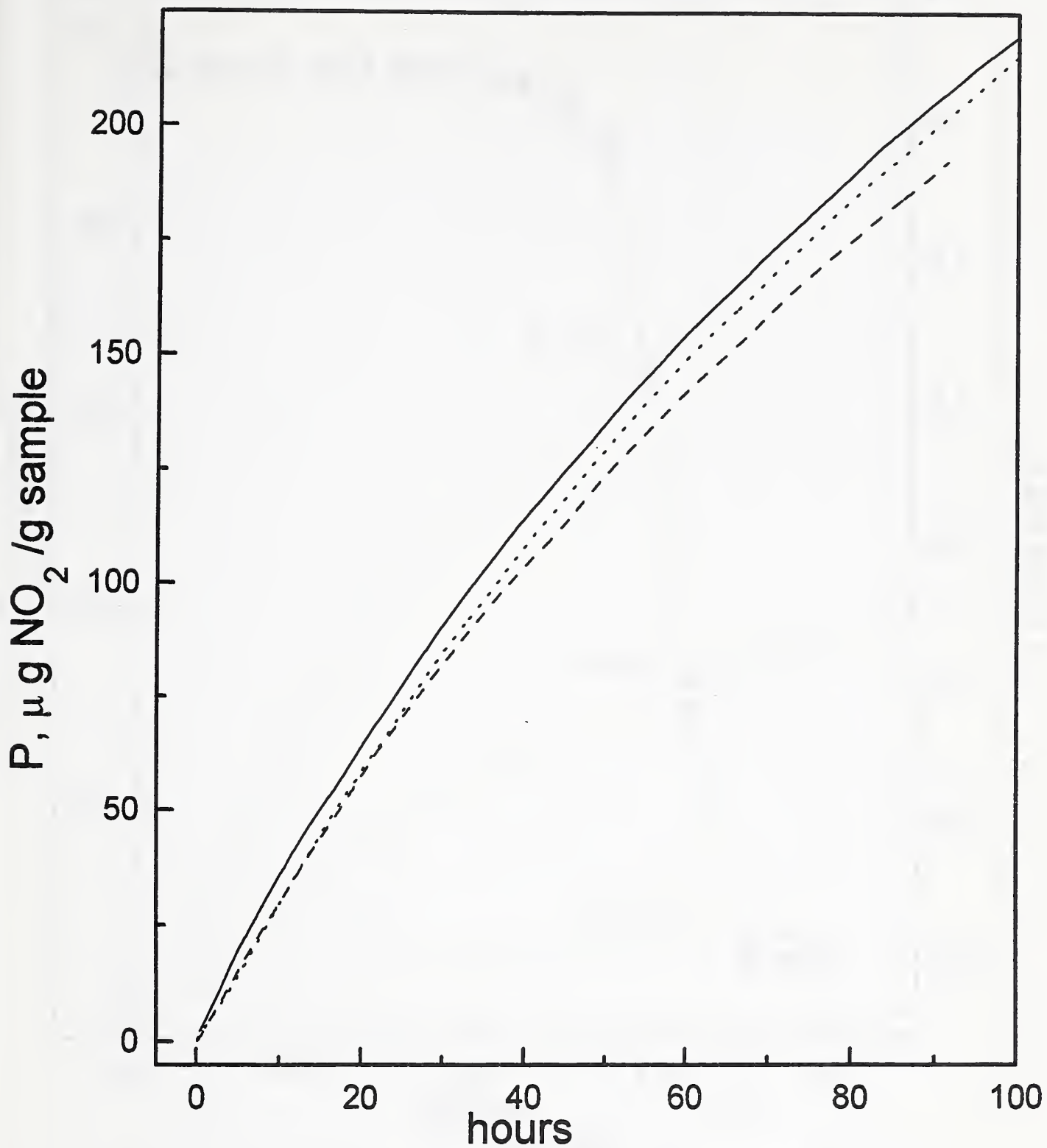


Fig 5. Repeats of board NARA B at about 8 $\mu\text{L/L}$ reference.

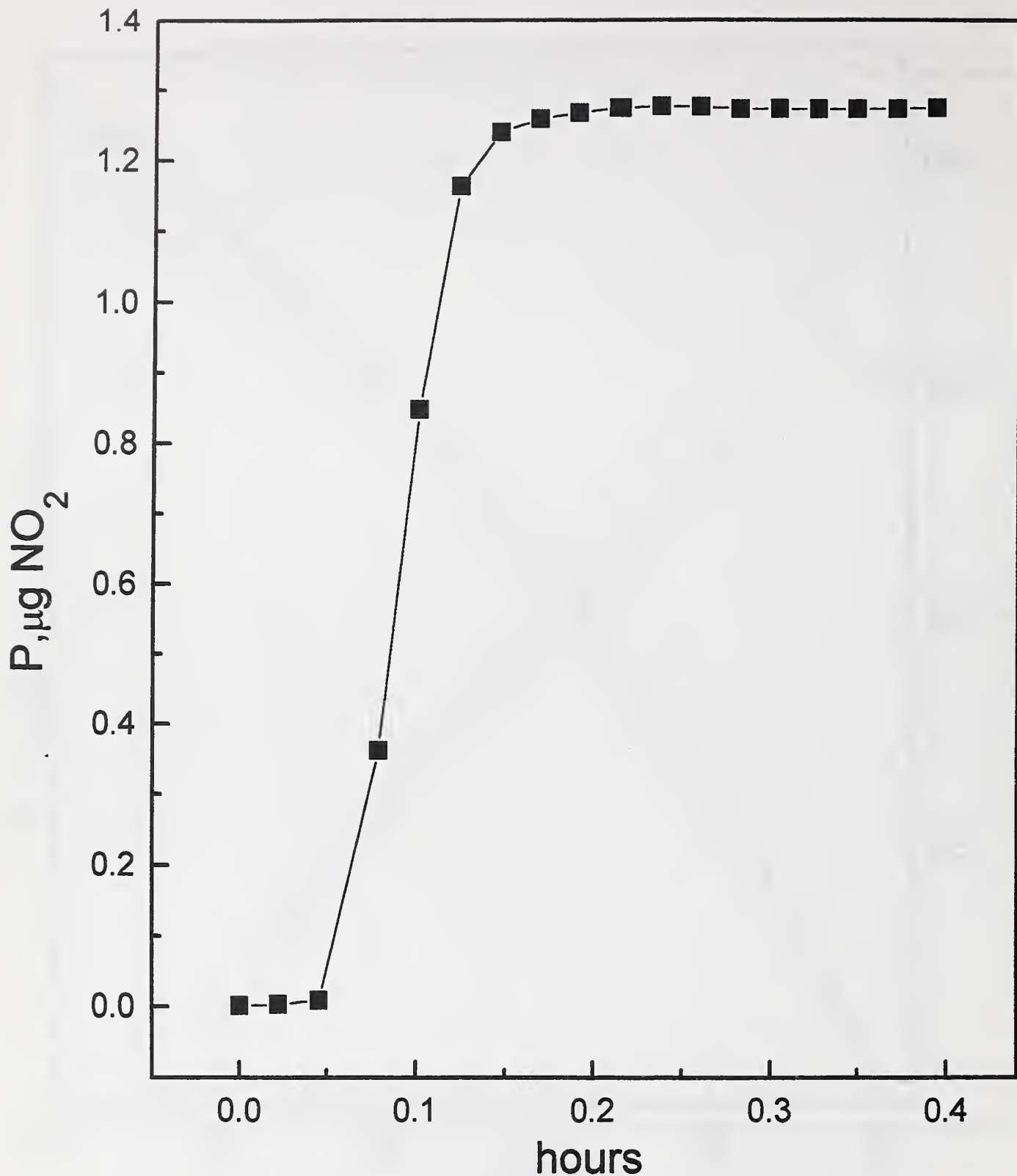


Fig 6. Loss of NO_2 gas as a result of opening and closing closing the apparatus without putting in sample. This lost pollutant gas appears as absorbed NO_2 in the experiments.

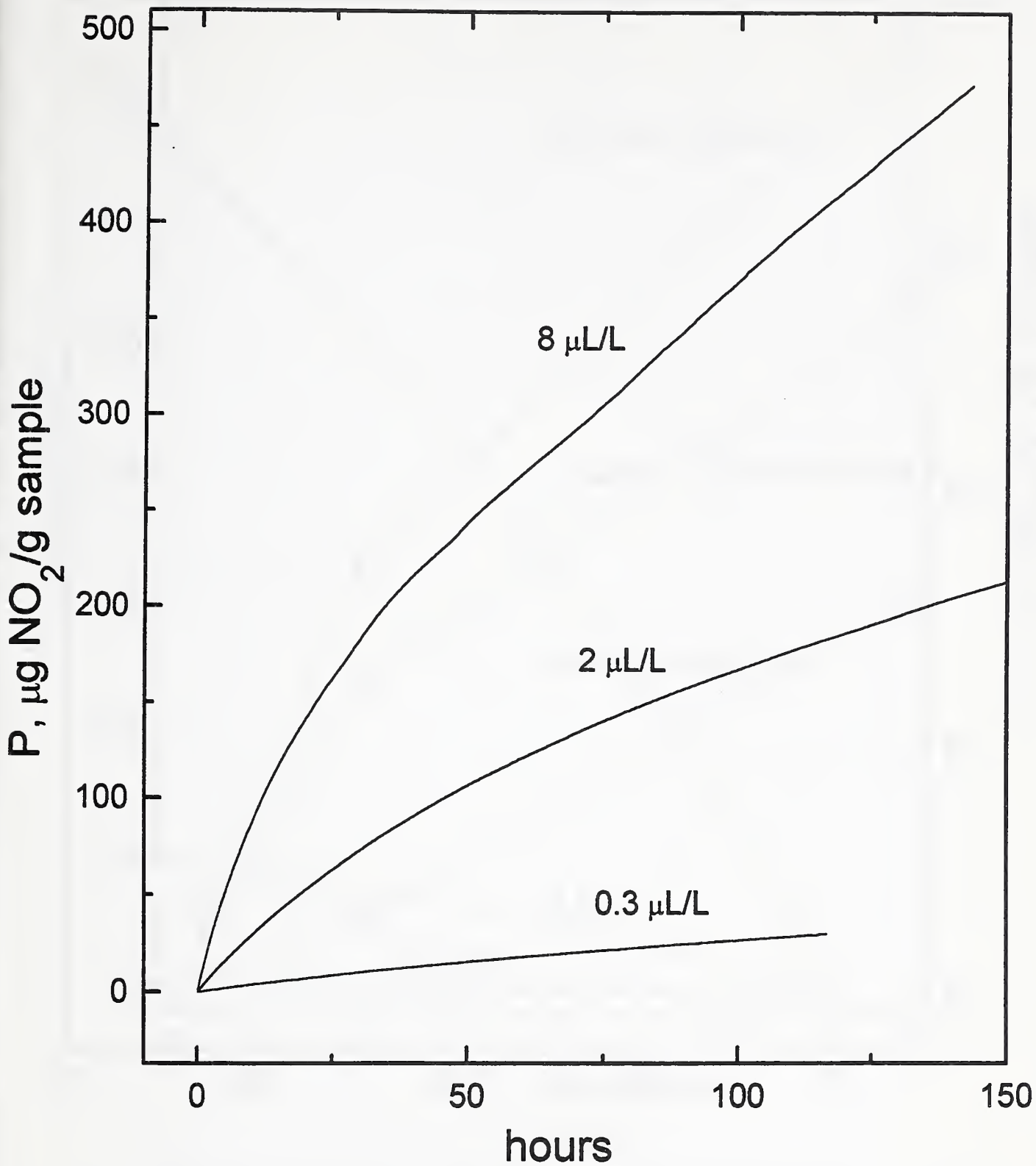


Fig 7. Absorption, P , of NO_2 as a function of time at various reference concentrations of NO_2 for sample NARA A .

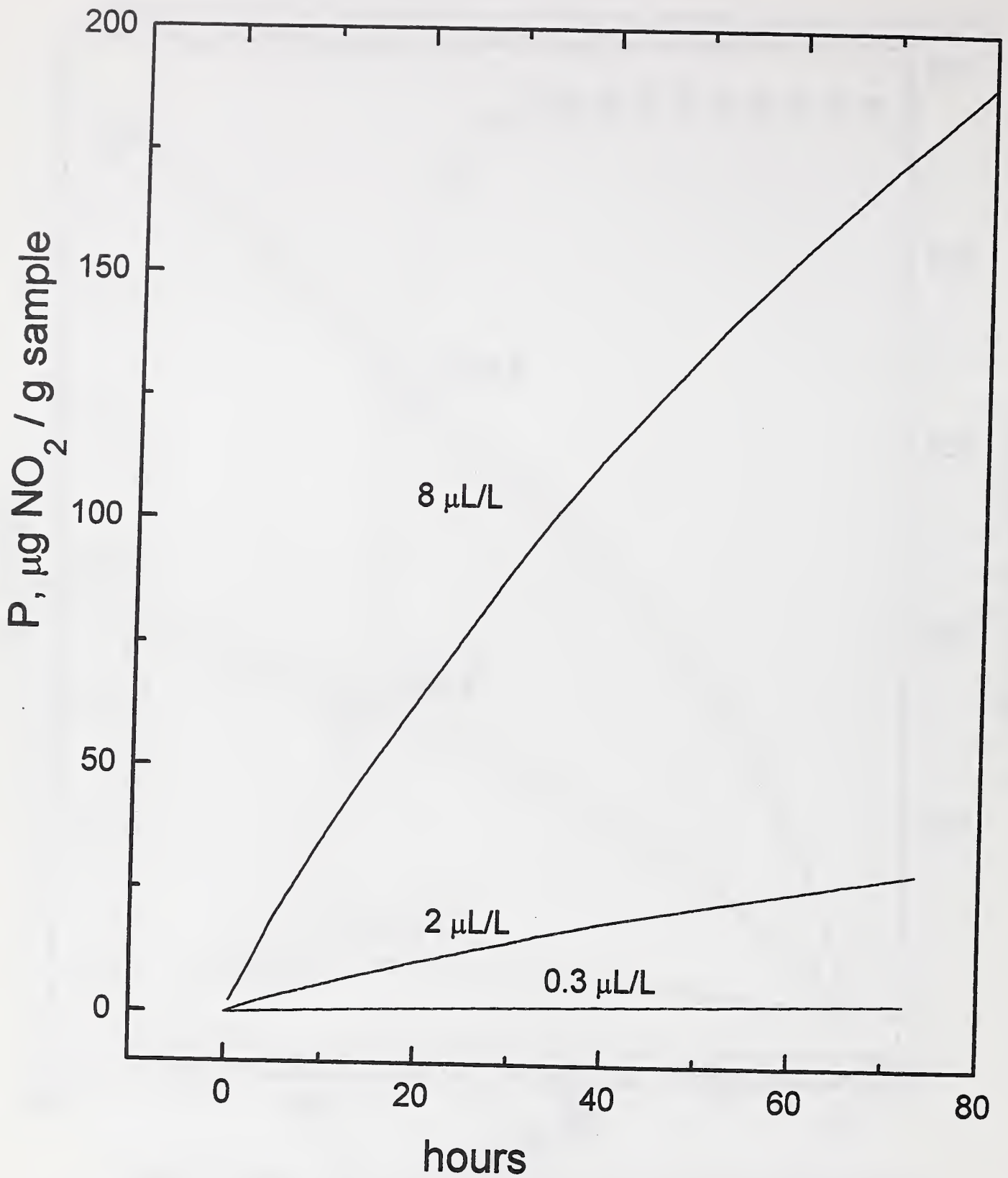


Fig 8. Absorption, P , of NO_2 as a function of time at various reference concentrations of NO_2 for NARA B.

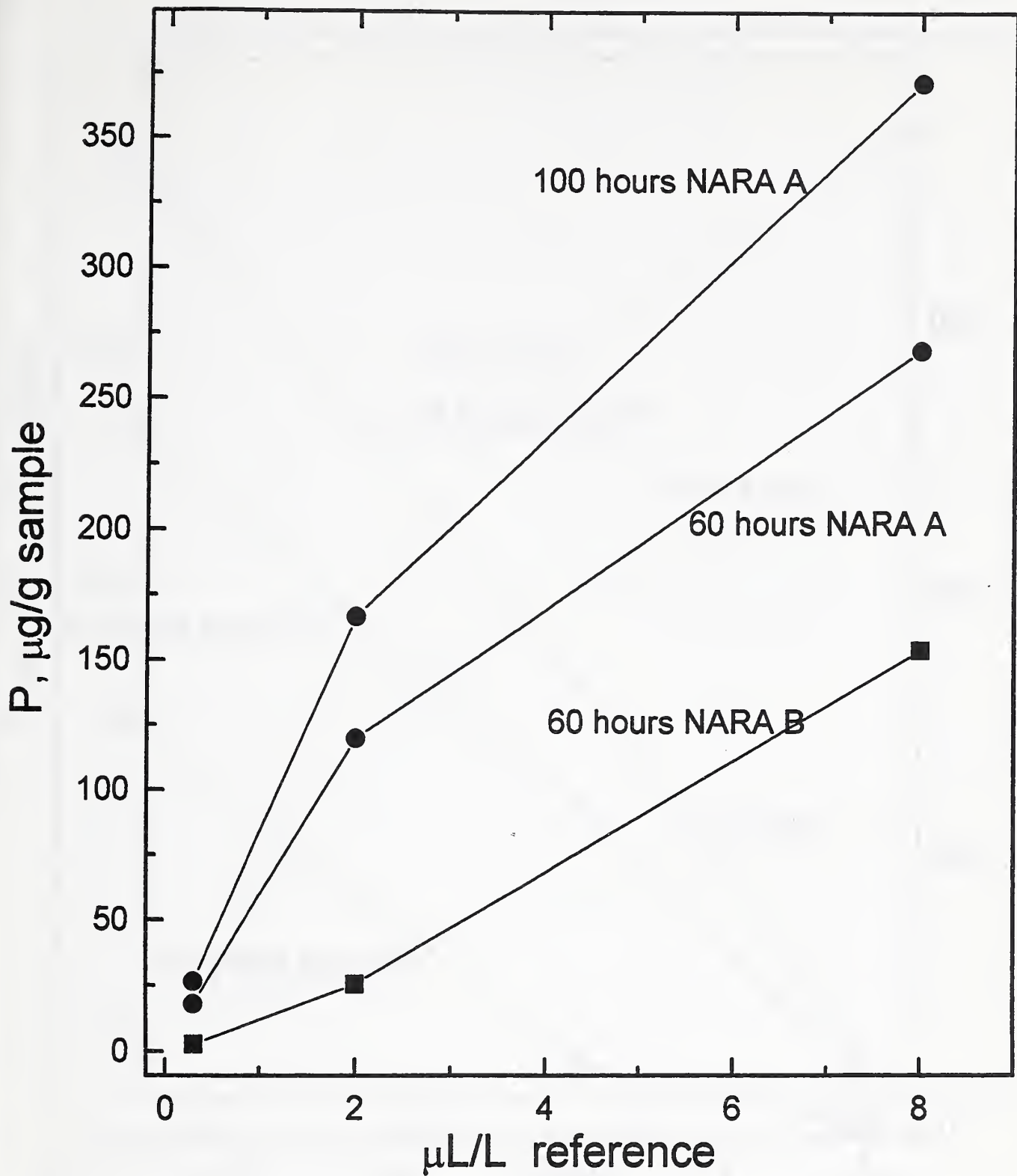


Fig 9 Plot of NO_2 reference concentration versus absorption, P , for NARA A and B boxboards at 60 and 100 hours. The absorption of the NARA B boxboard is nearly linear in reference concentration, The absorption of NARA A is not linear in reference concentration.

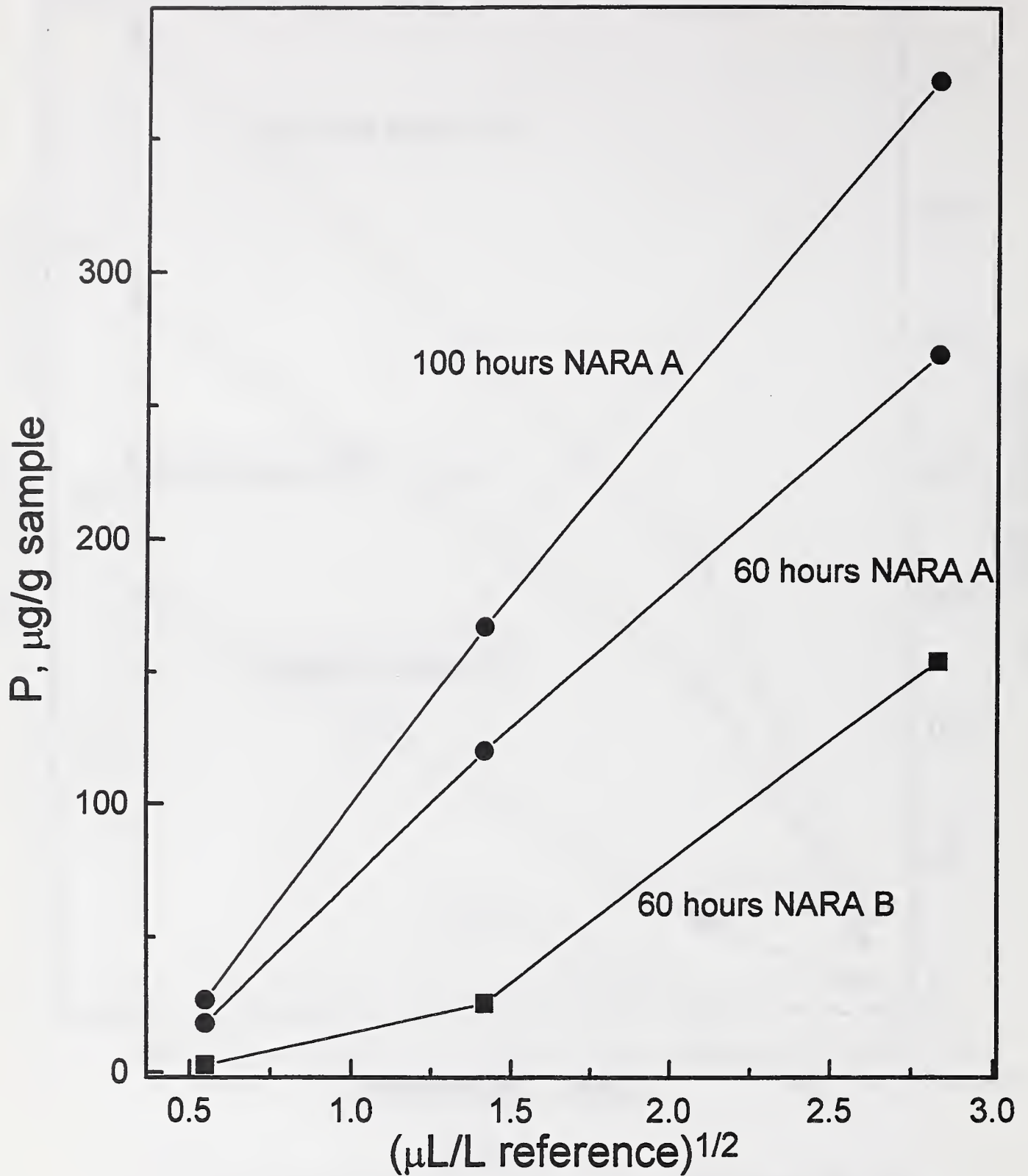


Fig 10 Plot of square root of the NO_2 reference concentration versus the absorption, P, at 60 hours and 100 hours for NO_2 absorption of NARA A box board and 60 hours for NARA B boxboard.

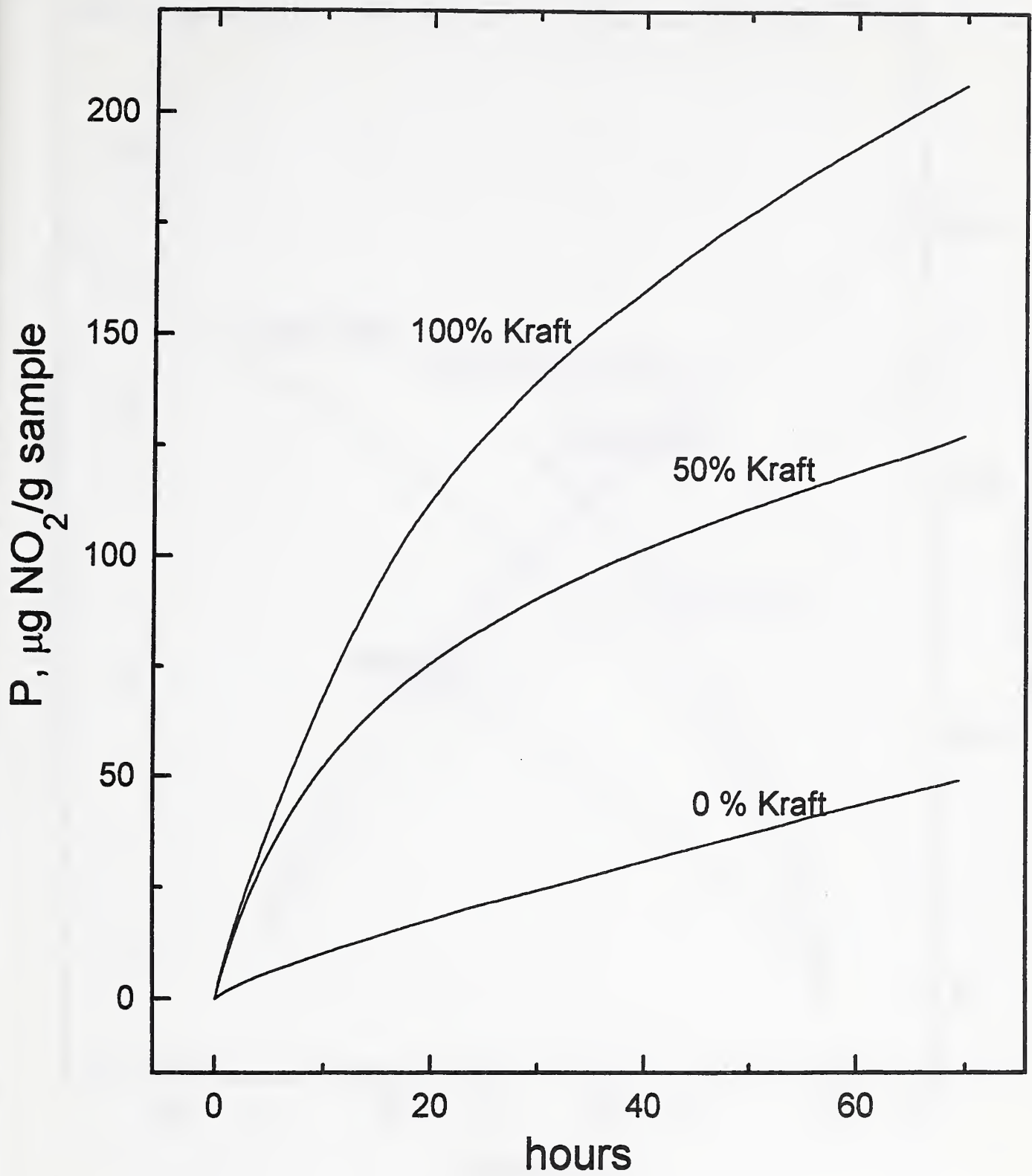


Fig 11 . Effect of percent Kraft on NO₂ absorption at 2 µL/L reference.

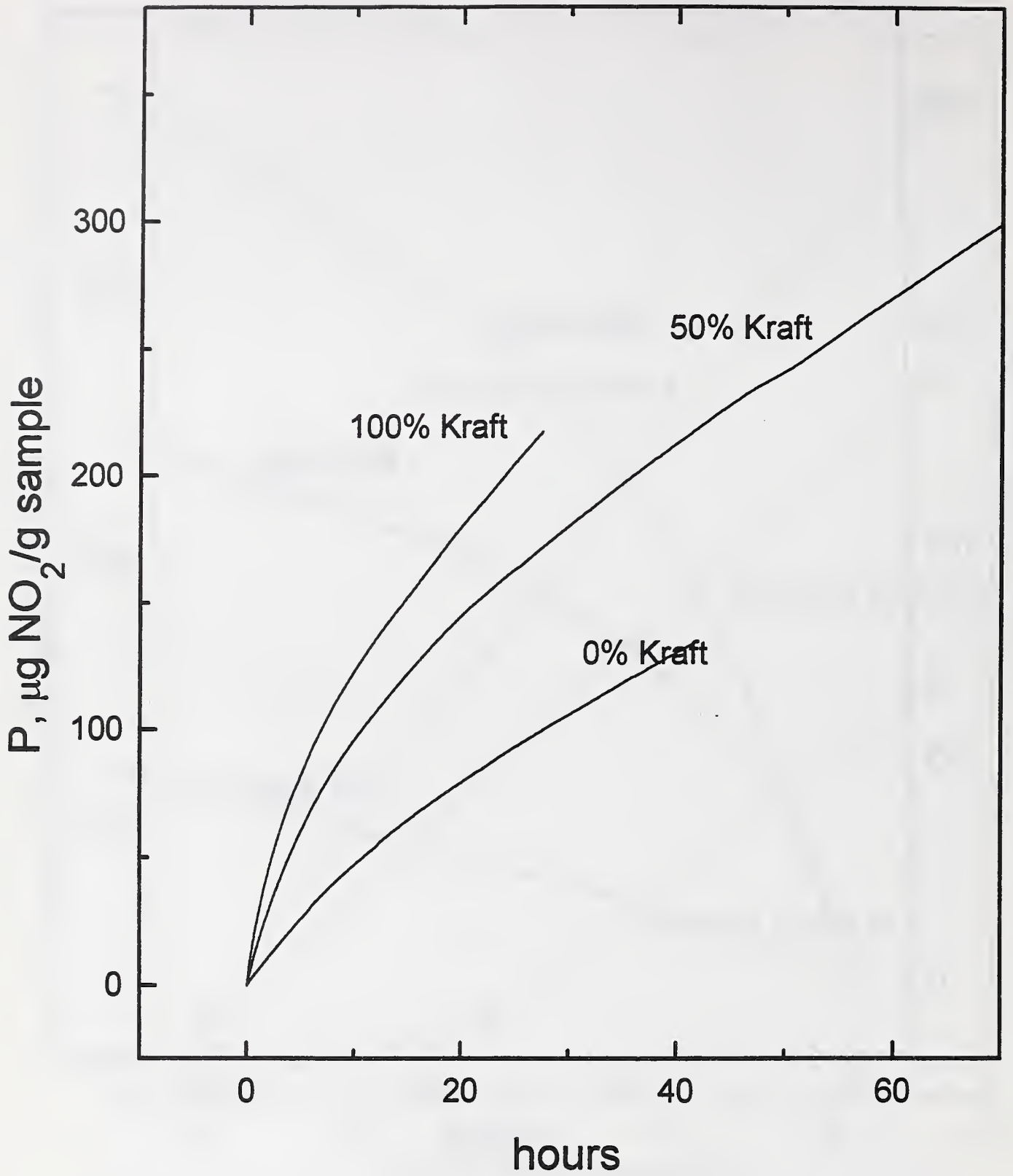


Fig 12. Effect of percent Kraft on NO₂ absorption, P, at 8 μL/L.

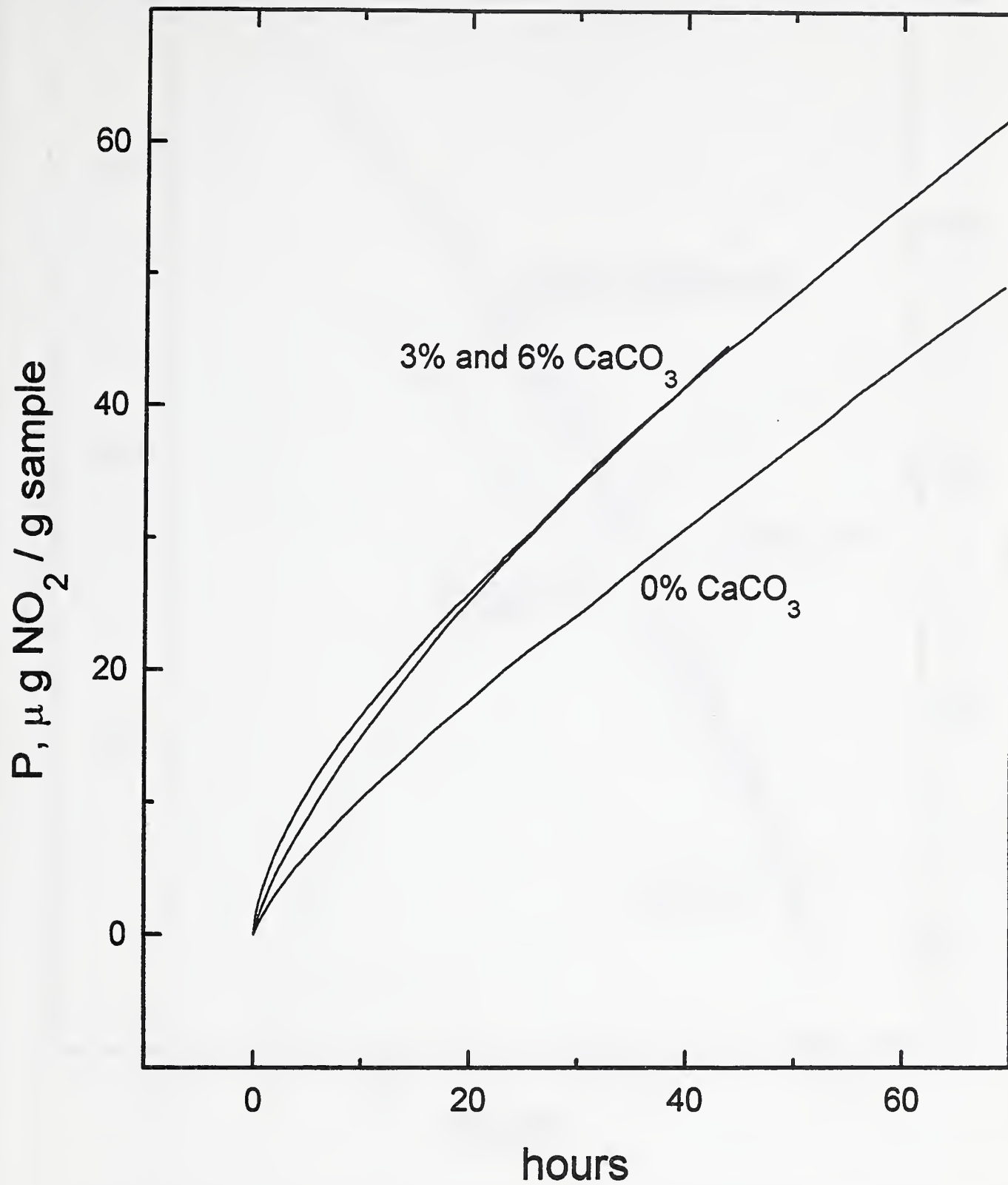


Fig 13. Effect of CaCO_3 on NO_2 absorption, P, at $2 \mu\text{L/L}$.

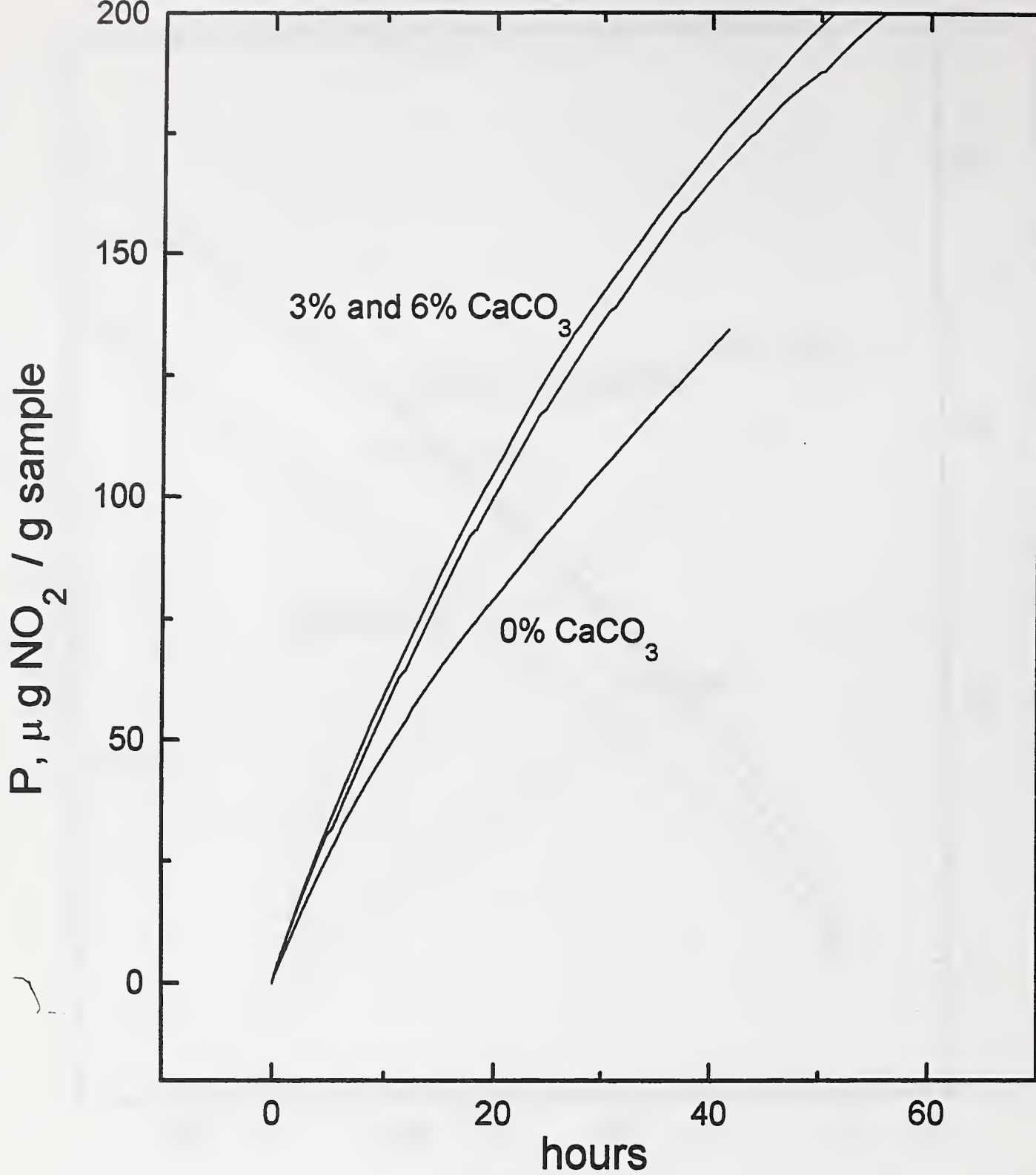


Fig 14. Effect of CaCO_3 on NO_2 absorption, P at 8 $\mu\text{L/L}$ reference.

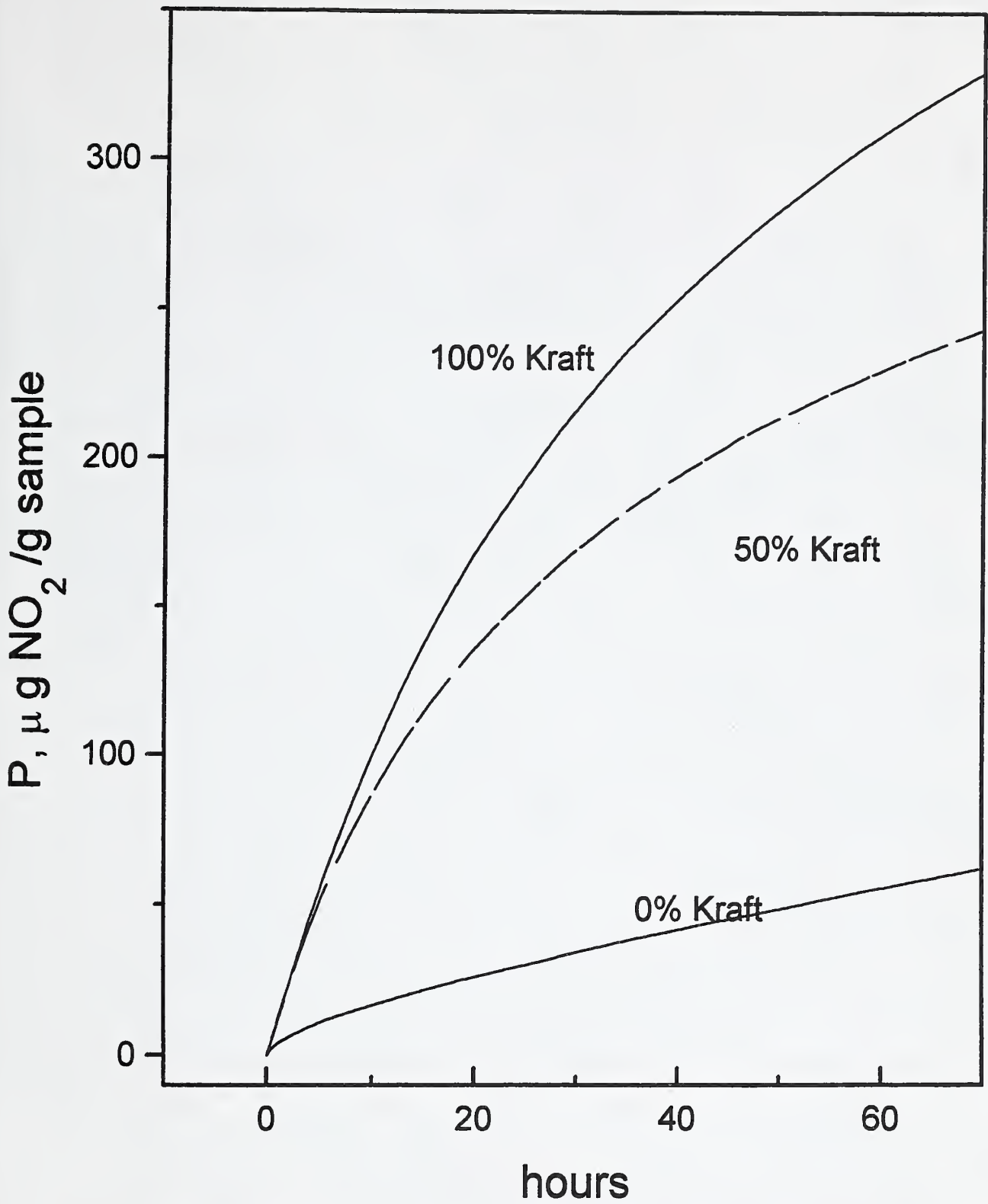


Fig 15. Effect of percent Kraft on NO₂ absorption, P, at 2 μL/L reference NO₂. Sample has additional CaCO₃.

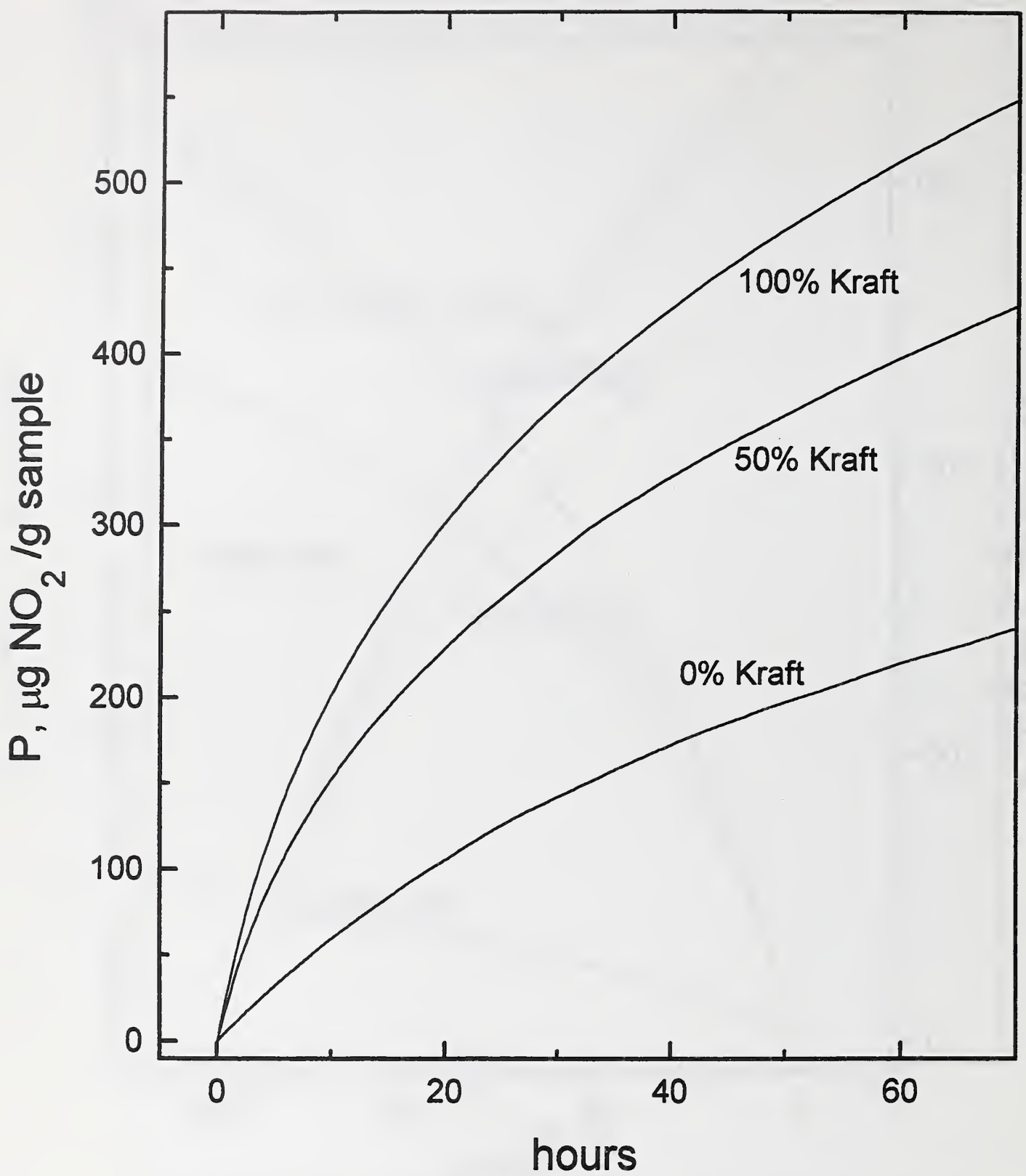


Fig 16. Effect of percent Kraft on NO₂ absorption, P, at 8 μL/L reference NO₂. Samples have additional CaCO₃.



