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Odor Assessment for Sewage Sludge Samples 300A01002

Donna B. Cash
Peter M. Molton

December 1976

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Pacific Northwest Laboratories

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ODOR ASSESSMENT FOR SEWAGE SLUDGE SAMPLES

300A01002

by
Donna B. Cash
Peter M. Molton

December 1976

BATTELLE
Pacific Northwest Laboratories
Richland, Washington 99352

SUMMARY

This is the final report on a research project performed by Battelle's Pacific Northwest Laboratories (PNL) for Sandia Laboratories. The objective of the project was to determine if the odor of digested and undigested sewage sludge (using a dilution-to-threshold test) changed over a seven-day period. Both treated and untreated sludge samples were evaluated. The treatment, performed by Sandia Laboratories in their facilities, consisted of a combination of irradiation and heat. In addition, PNL was to determine if gas chromatography (GC) was an adequate technique for qualitative identification of sewage sample head-space vapor components, and for monitoring their variation over time.

It was found that the odor of both treated and untreated undigested sewage sludge changed significantly over the seven-day testing period. The odor of treated undigested sewage sludge was stronger than the odor of untreated undigested sewage sludge. Although the maximum threshold odor number (T.O.N.) did not occur on the same day for all the samples, the odor pattern of an increase until a maximum was reached, then a slight decrease or leveling off of the odor, tended to occur for all the samples.

The odor of digested sewage sludge also changed significantly over the testing period. The odor of treated digested sewage sludge was stronger than the odor of untreated digested sludge except in one instance where it was the same. The maximum T.O.N. for treated digested sewage sludge was 683,000 while the maximum T.O.N. for untreated digested sludge was only 190,000. The odor of digested sewage sludge, both treated and untreated, increased until a maximum was reached.

The detection of sewage volatiles is practicable by GC using an electron capture detector but not using a flame ionization detector. GC results indicated a difference between digested and undigested samples of sewage sludge as well as small differences

between treated and untreated samples. All components of sewage volatiles detected showed a time variation with a distinct maximum after air exposures of two to four days.

In addition, it was determined that collection of individual GC peaks for odor testing is possible. Also, hydrogen sulfide was identified as one sewage odor component.

It appears that of the three components that were identified in the GC analysis peak B was an odoriferous component. Peak B might be useful in determining the odor strength of undigested sewage sludge. However, no conclusions can be drawn on the degree of influence that peaks A and C exert on the odor of the sewage sludge studied, and further investigation would be necessary in order to draw any firm conclusions.

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by

Donna B. Cash
and
Peter M. Molton

INTRODUCTION

Sandia Laboratories is investigating the use of radiation as a means of detoxifying sewage sludge as an alternate to the more conventional biological digestion treatment method. A combination of gamma irradiation and heat (thermoradiation) treatment is being studied by Sandia Laboratories. In support of this effort, Battelle's Pacific Northwest Laboratories (PNL) was requested to assess the odor change of the sewage sludge, if any, that occurs with time after the samples have been subjected to the treatment conditions.

Sewage sludge samples were provided to PNL by Sandia Laboratories. Samples consisted of four different treatments:

a) digested irradiated sewage - A
b) digested untreated sewage (control) - B
c) undigested (raw) irradiated sewage - C
d) undigested (raw) untreated sewage (control) - D

PNL agreed (Contract Number 300A01002--"Odor Assessment for Sewage Sludge Samples")--to perform comparative odor testing on these samples, allowing the samples to stand exposed to room air for from 24-168 hours before testing by the dilution-to-threshold odor panel method described in the text. Results of the dilution-to-threshold test were to be used to answer the following questions.

1. Does any change occur in the odor of the sewage sludge samples with time?
2. Is any apparent change in sample odor statistically significant?
3. If the sample odor does change with time, when does that change occur?
4. Is there any difference in sample odor as the direct result of the thermoradiation treatment?

In addition, PNL was to determine if gas chromatography could be used as a chemical method for detecting sewage odor components and, if so, to use this method to monitor any time variation in intensity of these components in the samples. Results of the chromatography analyses were to be correlated with the results of the dilution-to-threshold odor panel tests.

The detailed results follow in three separate sections. The first section presents the experimental procedure used and the results of the odor panel evaluation. The second section describes the development of a gas chromatography technique to measure the components of sewage sludge head space vapors and discusses the results of sample chromatograms obtained. The third section of the report correlates the results of the odor panel evaluation and the gas chromatography measurements.

ODOR PANEL ANALYSES

EXPERIMENTAL PROCEDURE

A dilution-to-threshold test was used to determine the odor intensity of the samples. The test is outlined in Standard Methods for the Examination of Water and Wastewater.[a] This test determines the ratio by which an odor-bearing sample has to be diluted with odor-free water for the odor to be just detected by the panel member. This dilution ratio is called the "threshold odor number" (T.O.N.); the higher the T.O.N., the stronger the odor of the sample.

The sewage sludge samples studied were prepared by and hand-delivered to Battelle's Pacific Northwest Laboratories (PNL) by Sandia Laboratories personnel. The sludge samples consisted of four sewage treatments.

A. Digested irradiated and heated sewage.
B. Digested untreated sewage (control).
C. Undigested (raw) irradiated and heated sewage.
D. Undigested untreated sewage (control).

Five samples of each of the four treatments were furnished for a total of 20 sludge samples when the samples were delivered to PNL. Four of the samples from each treatment (16 total bottles) were placed in a freezer for storage. The freezer temperature was maintained at $0^{o}C$. One sample from each of the four treatments was placed in a separate porcelain dish and allowed to evaporate in a hood over the 7-day testing period to simulate drying bed conditions. Each treatment was evaluated on day 1 (24 hours old from time of irradiation treatment), also on days 2, 3, 4, and 7 for a total of five testing days.

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a. Standard Methods for the Examination of Water and Wastewater, American Public Health Association, American Water Works Association, Water Pollution Control Federation (14th ed.), part 206, pp. 78-82, 1975.

Two treatments were evaluated in the morning and two in the afternoon on each test day. Treatments were randomly evaluated to eliminate the possibility that one treatment would always be tested in the afternoon or that one treatment would always be compared with the same other treatment.

All dilutions of the sewage samples were performed with odor-free water. The odor-free water was obtained by passing distilled water through a Millipore system. The schematic for this system is shown in Figure 1. This system produces reagent grade water by first passing the water through a prefilter cartridge; then through an activated carbon cartridge to remove dissolved organics; third, through two deionization cartridges to remove dissolved inorganics; and, finally, through a membrane filter unit to remove all microorganisms and particles larger than 0.22 micrometers.

The resistivity of output water is between 10 and 18 megohm-cm. The odor of the water was sniffed daily by the investigators and no odor was noted.

For each panel, samples were prepared by removing the predetermined amount of sewage sludge from the porcelain evaporating dishes and diluting the sludge with the odor-free water. Aliquoting of sludge samples was done using sterilized 10 ml calibrated pipets that were disposed of after each use to eliminate any cross-contamination of samples. Because the sewage sludge was much too thick to go through the tip of the pipets, the tip was removed and amounts of sludge measured using the calibrations on the pipet. For larger dilutions 10 mls of sample were diluted in a volumetric flask to 1000 mls. Aliquots of this dilution, 8.3, 5.7, 4, 2.8, 2, 1.4, 1 mls were diluted to 200 mls, volumetrically, to yield T.O.N.'s of 2400; 3500; 5000; 70,000; 10,000; 14,000; and 20,000 respectively. Additional dilutions were made to obtain higher T.O.N's. All dilutions used are listed in Table 1.

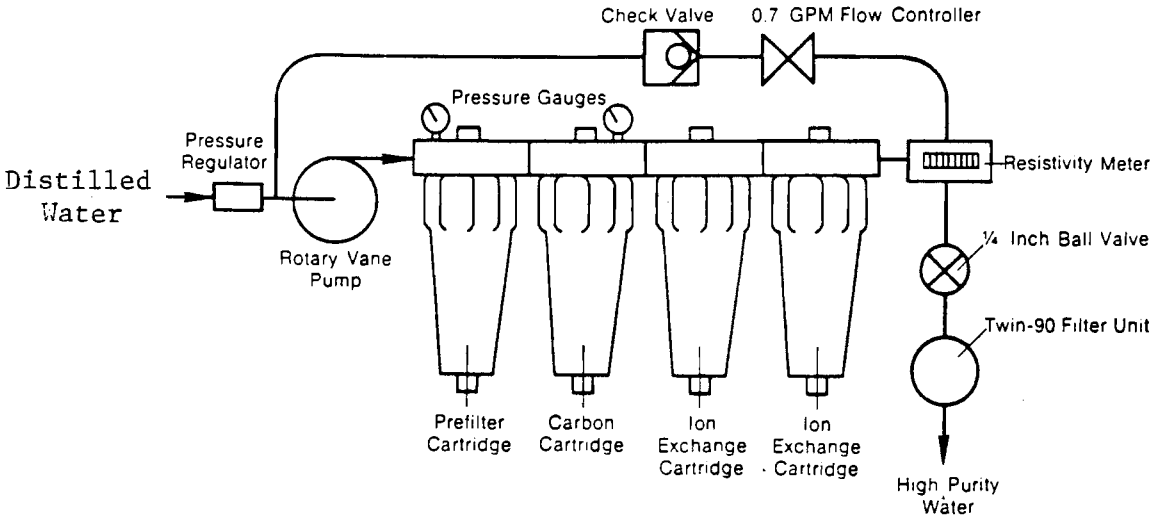

FIGURE 1. Schematic for the Millipore Water Filter System

TABLE 1. Threshold Odor Numbers (T.O.N.) Corresponding to Various Dilutions

Volume of Sewage Sludge Diluted to 1000 mls with Odor-Free Water					
10 ml		1 ml		0.1 ml[a]	
Aliquots Diluted to 200 mls	T.O.N.	Aliquots Diluted to 200 mls	T.O.N.	Aliquots Diluted to 200 mls	T.O.N.
8.3	2,400	8.3	24,000	8.3	240,000
5.7	3,500	5.7	35,000	5.7	350,000
4.0	5,000	4.0	50,000	4.0	500,000
2.8	70,000	2.8	70,000	2.8	700,000
2.0	10,000	2.0	100,000	2.0	1,000,000
1.4	14,000	1.4	140,000	1.4	1,400,000
1.0	20,000	1.0	200,000	1.0	2,000,000

a. 0.1 ml of sewage sample was obtained by a 10 ml aliquot from the 1 ml/1000 dilution since accurately measuring 0.1 ml of sewage sludge would have been extremely difficult.

Each panel member sniffed 5 dilutions and 2 blanks (200 mls of odor-free water) for each treatment for a total of 14 samples at each sitting. Samples were presented to the panel member in order of increasing concentration for each treatment. Blanks were randomly inserted in each series and were not identified for panel members.

Odor panels were conducted in a soundproof panel booth. The booth had a filtered air supply that was separate from the air supplied to the labs. The location of the panel booth was not in the same laboratory as that where sample preparation occurred. Panel members were not exposed to the sewage odor prior to sniffing. Odor panel testing began at 10:00 a.m. and again at 2:00 p.m. Only one panel member was in the booth at a time. The order in which panel members followed one another was random. Panel members were not allowed to smoke, eat or drink anything other than water one hour prior to sniffing. Panel members and experimenters did not wear perfumes or shaving lotions or use scented soaps for the duration of the test.

Preliminary experiments were conducted with twelve people. Eight people were chosen from this group as panel members for the actual testing. Although a panel of five-six members is recommended for precise work, eight were used in this case to allow for absences which might occur because of sickness or travel commitments during the course of the testing. Of these eight the values of six panel members were used in the final analyses.

The T.O.N. was determined for each panel member. The average T.O.N. for the six panel member group was then calculated and used as the T.O.N. for that particular sample.

Analysis of variance for each replication was conducted to determine if the indicated differences in T.O.N.'s were statistically sifnificant. The experimental design used was a randomized

complete block design.[a] In this analysis the variation of all data is broken down into three parts: (1) the variation between judges, (2) the variation with time (between testing days), and (3) the residual variation not accounted for as variation between judges or with time. This last variation is a measure of total unexplained variation in the experiment.

In addition, percent dry solids determinations were performed on digested and undigested sewage sludge samples. Samples were weighed and allowed to dry overnight in a vacuum drying oven set at 80°C. After removal from the oven, the samples were cooled in a dessicator approximately one hour and reweighed. The percent dry solids was then calculated as net dry weight/net wet weight x 100.

Discussion of odor panel results will be in two parts:

A. Results of undigested sewage sludge.
B. Results of digested sewage sludge.

RESULTS AND DISCUSSIONS

As explained in the Standard Methods for the Examination of Water and Wastewater, the threshold odor number (T.O.N.) is not a precise number. It will only approximate quantitative measurements of odor intensity. A different group of people would have a different odor threshold and, therefore, a different threshold odor number (T.O.N.). The results of a panel are more meaningful because individual differences have less influence on the result. Also the use of statistical analysis will determine if the indicated differences in T.O.N.'s are truly significant.

There are two inherent disadvantages to the dilution-to-threshold test. First, the dilution method is based on the

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a. M. A. Amerine, R. M. Pangborn, E. B. Roessler, Principles of Sensory Evaluation of Food, Academic Press, New York, NY, 1965.

tenuous concept that the effect of dilution is a straight-line function of concentration of the test product in an odor-free vehicle and that all the products, despite differences in odor characteristics, will be affected identically by the vehicle. Also the effect of the test diluent is disregarded. Even though the diluent (odor-free water) has no recognizable odor, it may change the character of the test product.[a] Results from the dilution-to-threshold test will indicate trends but are not quantitative measurements. The reader must not treat the T.O.N.'s as quantitative numbers.

Preliminary Work

Preliminary odor testing was conducted to qualify Battelle's Pacific Northwest Laboratories (PNL) personnel to participate on the odor panel. Preliminary sewage sludge samples were furnished to PNL by Sandia Laboratories. Twelve people were screened and tested for their ability to sniff the odor of sewage sludge and to repeat their results. Of these twelve people, six were selected as panel members or judges. In addition, two other people, lesser qualified, participated in the odor panel to insure that there would always be six total panel members in case some one panel member had to be absent because of sickness or some other unforeseen circumstance. Fortunately, this did not occur and the results of the original six judges were used for statistical analysis.

Preliminary sewage sludge samples were also used to determine the odor threshold range, that is, what dilution of the sewage sludge would be needed to include the threshold range of all the panel members, also how much the dilution should be increased each day so that the total number of samples (5) tested each day for each treatment would still include the panel's threshold range as well as test any time variation in odor that might occur.

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a. M. A. Amerine, R. M. Pangborn, E. B. Roessler, Principles of Sensory Evaluation of Food, Academic Press, New York, NY, 1965.

The T.O.N.'s of preliminary sewage sludge samples furnished to PNL by Sandia Laboratories were in the range of 3,500 to 10,000. Samples seemed to change slightly over the time the preliminary work was being conducted. However, since the panel was also being qualified, it was not possible to determine if the change was caused by sewage odor variations or by improved ability on the part of the panel members to identify the odor.

Undigested (Raw) Sewage Sludge

Average T.O.N.'s of the six panel members for treated and untreated raw sludge samples are given in Table 2 for each of the three replications. Individual panel member's T.O.N.'s are listed in Appendix A.

Because the sludge that was furnished to PNL by Sandia Laboratories for actual testing did not have the same odor strength as the samples that were provided for the preliminary work, the sewage sludge dilutions for the first replication were not in the range of the panel's threshold. Except in two cases (day 7 treated and day 3 untreated) judges could either smell odor in all of the diluted samples--which means the T.O.N. should be higher than indicated--or could not smell odor in any of the samples, which meant the T.O.N. should be lower. For this reason the data from Replication I were not statistically analyzed, as it would have biased the results.

Results of the statistical analysis for Replications II and III are listed in Appendix A. Although the T.O.N. for each day was not significantly different from the T.O.N. of every other day for both treated and untreated undigested sewage sludge, there were significant odor differences that occurred.

The T.O.N. of undigested treated sewage sludge reached a maximum of 683,000 on day 4 for Replication II. This maximum odor was significantly greater than the odor of all the other days. For Replication III the maximum T.O.N. occurred on the

TABLE 2. Average[a] Threshold Odor Numbers for Raw (Undigested) Sewage Sludge

	Treated			Untreated		
	Replication			Replication		
Day	1	2	3	1	2	3
1	>14[b]	>70	160	>14[b]	41	51
2	>24	217	272	>70	128	89
3	>70	>350	207	70	158	118
4	>350	683	147	<350	237	165
7	402	220	140	<200	193	78

a. Average of six individual judges' scores.
b. Threshold odor numbers are in thousands, i.e., day 1 > 14,000.

second day (272,000) and although this T.O.N. was not significantly different from the T.O.N. of the third day (207,000), it was significantly higher than all the other days.

In general, the odor of undigested treated sewage sludge changed significantly over the seven-day testing period. The odor reached a peak on or before the fourth testing day and then decreased.

The T.O.N.'s for untreated undigested sewage sludge were lower in all cases except one (Replication III, day 4) than the T.O.N.'s of treated undigested sewage sludge (Table 2). The maximum T.O.N. for treated undigested sewage was 683,000, while the maximum T.O.N. for untreated undigested sewage was only 237,000.

The odor of the untreated undigested sewage sludge changed significantly over the seven-day period, but like the treated undigested sewage sludge each day's T.O.N. was not significantly different from every other day's T.O.N.

The maximum T.O.N. for untreated undigested sewage sludge occurred on day 4 in both replications (Replication II - 237,000 and Replication III - 165,000). For Replication II the maximum T.O.N. was significantly greater than days 1, 2 and 3 but not day 7. In Replication III the maximum T.O. N. was significantly greater than days 1, 2 and 7 but not day 3. Thus, the odor of untreated undigested sewage sludge peaked around the third or fourth day and decreased slightly by the seventh day.

In summary, the odor of treated and untreated undigested sewage sludge changed significantly over the seven-day testing period. The T.O.N.'s of treated undigested sewage sludge were greater than the T.O.N.'s of untreated undigested sewage sludge. Although the maximum T.O.N. did not occur on the same day for all the samples, the odor pattern of an increase until a maximum was reached, then a slight decrease or leveling off of the odor tended to occur for all the samples.

The undigested sewage samples furnished by Sandia had 4.55% dry solids.

Digested Sewage Sludge

The initial digested sewage samples that Sandia Laboratories supplied to Battelle, Pacific Northwest Laboratories (PNL), were not typical as determined by Sandia. PNL was requested to discontinue analysis of these samples and additional digested sewage sludge samples were furnished at a later date. Because of time constraints, only two replications of these samples were conducted. One replication was performed in the morning and one in the afternoon.

Average T.O.N.'s for each replication are listed in Table 3. Individual T.O.N.'s for each panel member are given in Appendix A, as well as results of the statistical analysis.

Following the same pattern of undigested sewage sludge, the T.O.N. of treated digested sewage sludge changed significantly over the seven-day testing period. The maximum T.O.N. for both Replications I and II occurred on the third day. For Replication I the maximum T.O.N. of 683,000 of treated digested sludge was significantly higher than the T.O.N.'s of all the other days. For Replication II the maximum T.O.N. of 458,000 on day 3 was significantly higher than the T.O.N.'s of days 1, 4 and 7, but not day 2. The odor pattern for treated digested sewage sludge appears to have a slightly more abrupt peak than that for treated undigested sewage sludge.

The T.O.N.'s for untreated digested sewage sludge were lower than the T.O.N.'s for treated digested sludge, except in one instance, Replication II, day 7, where they were the same (Table 3). The maximum T.O.N. for treated digested sewage sludge was 683,000 while the maximum T.O.N. for untreated digested sludge was only 190,000.

TABLE 3. Average[a] Threshold Odor Numbers for Digested Sewage Sludge

	Treated		Untreated	
	Replication		Replication	
Day	1	2	1	2
1	32[b]	48	21	39
2	183	413	72	118
3	683	458	172	98
4	213	238	183	142
7	140	190	85	>190

a. Average of six individual judges' scores.
b. Threshold odor numbers are in thousands, i.e., day 1 - 32,000.

The T.O.N.'s changed significantly for digested untreated sewage sludge. The first replication followed the same trend as has been previously noted--an increase in T.O.N. followed by a decrease. The odor peak occurred on the third and fourth days (172,000 and 183,000). Although the T.O.N. values for these two days were not significantly different from each other, they were significantly greater than the T.O.N.'s for all the other testing days.

For some unexplained reason the second replication did not follow the same general pattern. The maximum T.O.N. was on the seventh day. This maximum was not significantly different from day 4 but might have been if there had been another higher dilution. Expecting the same pattern (an odor decrease on the seventh day) the five dilutions sniffed covered the T.O.N.'s of 50,000-200,000. Five of the six panel members could detect odor in all of the samples. The T.O.N. on day 7 was significantly different from the T.O.N. on days 1, 2 and 3. The sewage sludge that remained in the porcelain evaporating dish for digested treated sewage on the seventh day of Replication II was drier than any of the previous samples. When the sludge was destroyed after testing was completed on that day, it was particularly noticeable how dry the sample was. This may account in some manner for the change in odor pattern. However, more testing is needed.

Digested sewage sludge had an average of 11.4% dry solids for treated sludge and 12.2% dry solids for untreated sludge.

Conclusions

From the above results and discussions the following general conclusions can be made:

1. The odor of all sewage sludge investigated increased over a week's time span.

2. The odor increase is not a linear function with time.

3. Treated sewage sludge has higher T.O.N.'s (stronger odor) than untreated sludge for both digested and undigested sludge.

4. Although the T.O.N. is not a quantitative odor measurement, the odor pattern that occurred in the majority of cases was an increase in odor until a maximum occurred. This maximum was significantly higher than the initial odor of the sewage. The maximum was followed, generally, by a decrease in odor.

5. Undigested sewage sludge had 4.55% average dry solids and digested sewage sludge an average of 11.8% dry solids.

CHEMICAL ANALYSIS OF GASEOUS COMPONENTS

Separate research was performed to develop and use gas chromatography (GC) methods and equipment to fractionate and characterize changes in the odor components present in selected sewage sludge samples provided by Sandia Laboratories. This research was intended to be qualitative in nature only. That is, it was intended to (1) indicate the presence of the various chemical odor components, (2) indicate the trend in variations in concentration of the odor components with time, and (3) provide data for correlation with the results obtained from the odor panel experiments. Quantitative analysis and direct chemical identification of the individual odor components was not an objective of the research in this phase of the project.

METHODOLOGY DEVELOPMENT

Before starting on a detailed series of determinations in concert with the odor-testing panel research, it was necessary to determine under what conditions GC analytical techniques were sufficiently sensitive to detect sewage odor components, and to determine optimum conditions for routine work.

A Perkin-Elmer 900A GC fitted with dual flame ionization detectors was used initially. Although it was possible with some care to operate the instrument at its maximum sensitivity, no response was obtained to any of the various sewage odor component concentration techniques used; specifically to (1) a hexane extract, (2) direct head-space vapor sample, or (3) to the liquid condensate obtained by passing purified nitrogen through a 50 ml sewage sample and trapping the vapors in liquid nitrogen. The latter would have provided the most concentrated sample, consisting of a 30 min passage of N_2 and yielding approximately 5 µl of aqueous condensate, all of which was injected at once.

Based on initial experiments it was concluded that the flame ionization detection system was not sufficiently sensitive to measure the sewage odor components in the Sandia samples. Consequently, the GC was modified by installation of an electron-capture detector (ECD) equipped with a ^{3}H-impregnated foil. This type of detector is much more sensitive than flame ionization or hot wire (katharometer) detectors but, unfortunately, is more troublesome to use. Its major disadvantage in the present context is its great sensitivity to traces of water, resulting in a gradual increase in baseline noise, spiking, drift, and a decrease in sensitivity with time. It is not possible to inject aqueous solutions directly into a GC employing an ECD without rendering the detector useless. Another disadvantage, not serious in this project, is the absolute maximum operating temperature of 200°C.

After an initial adjustment and calibration period the ECD was made operable at an attenuation of x4 (x1 being the maximum sensitivity) although the noise level was so high that frequently clearer results were obtained at an attenuation of x40. At this sensitivity a few picograms of odor components could be detected. Since the instrument sensitivity is very great for S,N, P, or halogen-containing compounds, iodomethane was used as a standard. A 1 µl vapor sample of iodomethane, diluted by a factor of 10^{6}, gave an offscale peak at an attenuation of x40.

Various modes of operation were tried to optimize instrument response and range for sewage samples. Sparging 50 ml of sewage with an activated charcoal-cleaned nitrogen stream for 30 min, with collection of the vapors in liquid nitrogen, gave an aqueous condensate. This could not be injected directly into the GC. Extraction of this aqueous condensate with 250 µl of hexane and injection of the hexane solution gave no response. Presumably the odor components were too dilute or too water-soluble to be extracted. Extraction of sewage directly with hexane gave the same result. In the end, the simplest and most successful mode

was to take a head-space air sample and inject this directly into the GC. Over a period of time, the water vapor in these samples caused an increase in detector noise, but for a one-week period this was tolerable. For prolonged determinations cleaning of the detector would be required about every two weeks.

Having established that sewage odor components could be detected with an ECD, it was necessary to optimize the GC operating conditions to allow measurement of as many as possible of these in a typical run. Consequently, programmed runs were made up to 200°C (the maximum), and isothermal runs were performed at 50°C, 100°, and 150°. No additional components were eluted in detectable amounts at temperatures above 50°C. Good separation was obtained between the observed components at 50°C; thus, this temperature was chosen for subsequent experiments. This does not exclude the existence of odor-causing components which would be eluted at higher temperatures but simply includes those materials which are present in maximum amount and which elute at 50°C, whether or not they are responsible for sewage odor. The GC cannot directly differentiate between odoriferous and non-odoriferous components. It is conceivable that a minor component in terms of concentration could be responsible for a large portion of the odor simply because it has a strong odor per unit of concentration.

Having determined the optimum detector type and column temperature (column material, gas flow, etc., having been optimized on the basis of past experience), the GC was ready for routine determinations on the Sandia samples over the time period for air exposure of 24-168 hr in concert with the odor panel determinations.

Before this was done, a further analysis was performed using a Hewlett-Packard 5710A GC fitted with a flame photometer detector. This instrument was being used routinely to determine H_2S on another research program. Since it had been commented that the odor of sewage was reminiscent of H_2S, it seemed worth trying to

confirm this. Samples C and D head-space vapors (1.0 ml) were injected and sample D vapor was mixed with H_2S and injected. The results (Figures 2-4) clearly show the presence of H_2S in the sewage vapors, together with another component, which is probably SO_2. No other work could be done on this instrument as it was committed for use on the other research program. The samples taken corresponded to the first replication (week 1) of the odor panel work, on the fourth day (air-exposed for 96 hr, assuming a 24 hr exposure before sample receipt at PNL.

TIME VARIATION OF SEWAGE ODOR COMPONENTS

During the second replication of the odor panel testing a series of GC analyses were made as follows:

Using the standard conditions outlined above and described more fully on p. 45 (Appendix B), head-space vapor samples were injected directly into the GC. Each day 5 ml volumes of sewage samples A-D were removed from the porcelain evaporating dishes, inoculated into cleaned glass bottles and shaken. After standing for 5 min, a 0.5 ml gas sample of A was withdrawn in a gas-tight syringe and injected. The GC trace was monitored until the third component was eluted (peak 'C'). The syringe was dismantled and kept in air at 60°C during this time to evaporate any residual odors and adsorbates from the barrel. The procedure was repeated using a sample of B, C, and D, respectively, in that order. The attenuation was x4. Then the sequence was repeated, using 1.0 ml of vapors at an attenuation of x40. This provided two GC traces, with a response difference of x5, and also provided a way of checking for identity of response to two separate injections of the same samples.

The used bottles were emptied, washed thoroughly, and heated at 100°C in a vacuum oven overnight to remove traces of vapors adsorbed on the glass before being used for the next day's samples.

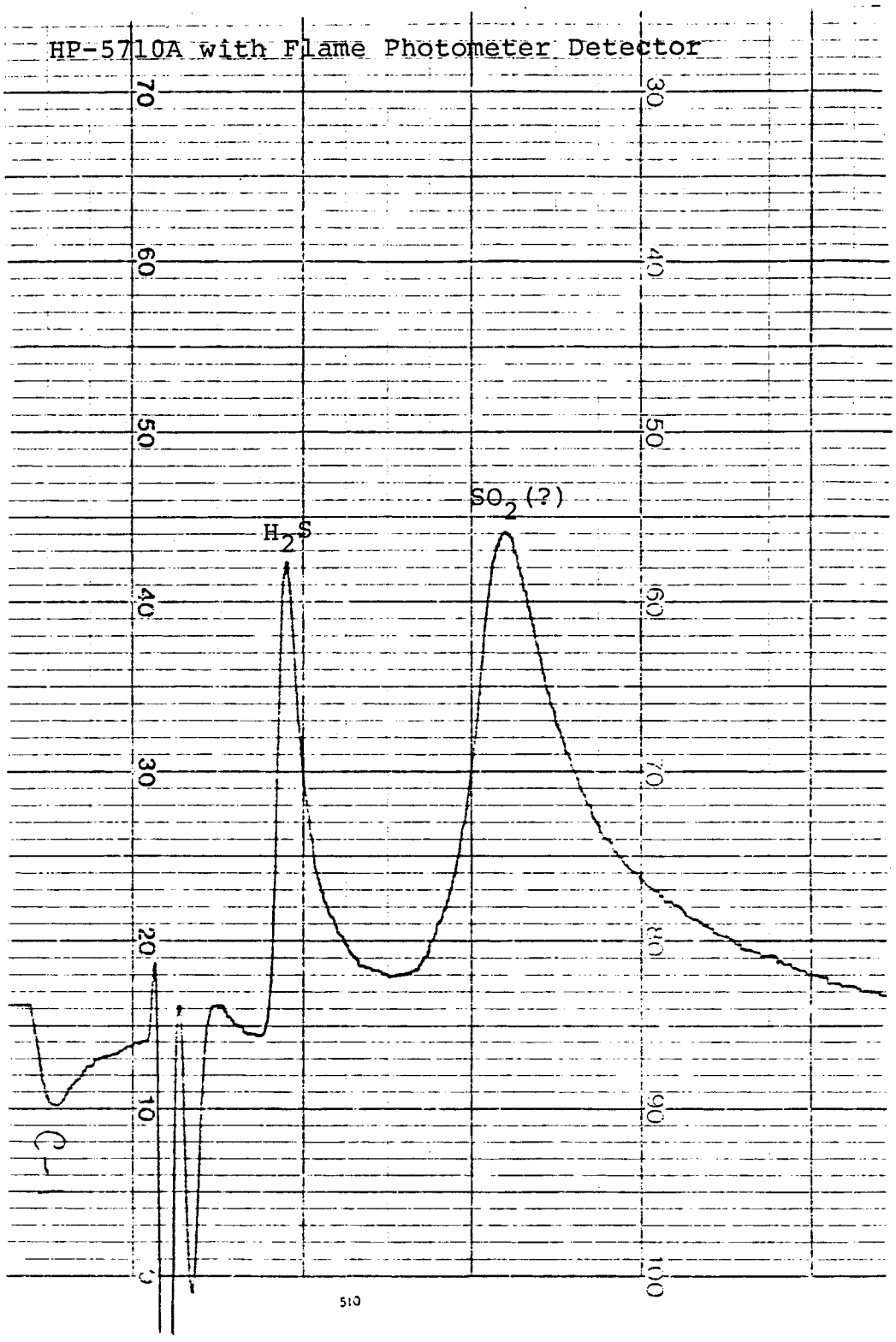

FIGURE 2. Trace of Undigested Treated Sewage Sludge (c); day 4 (96 hrs)

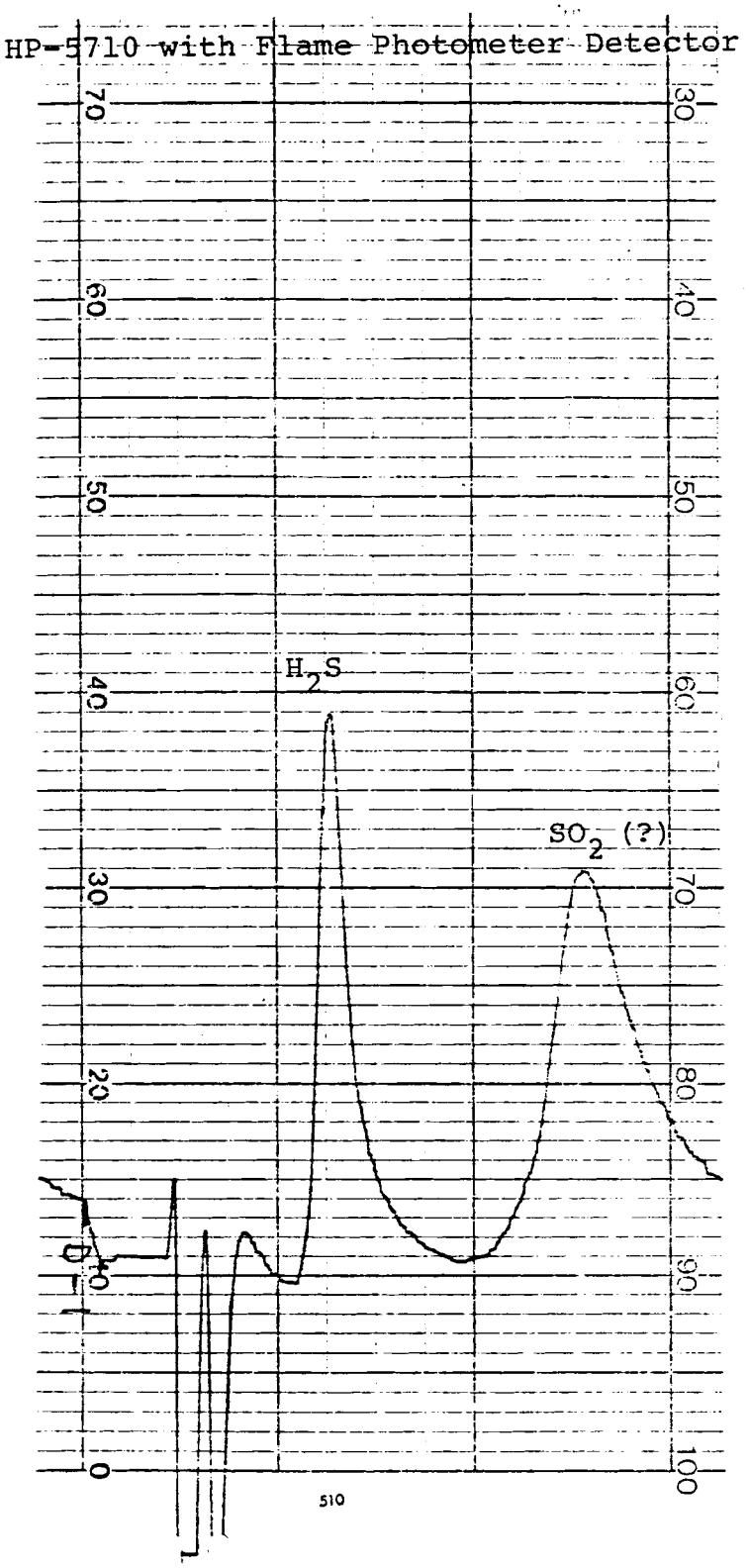

FIGURE 3. Trace of Undigested, Untreated Control (D); day 4 (96 hrs)

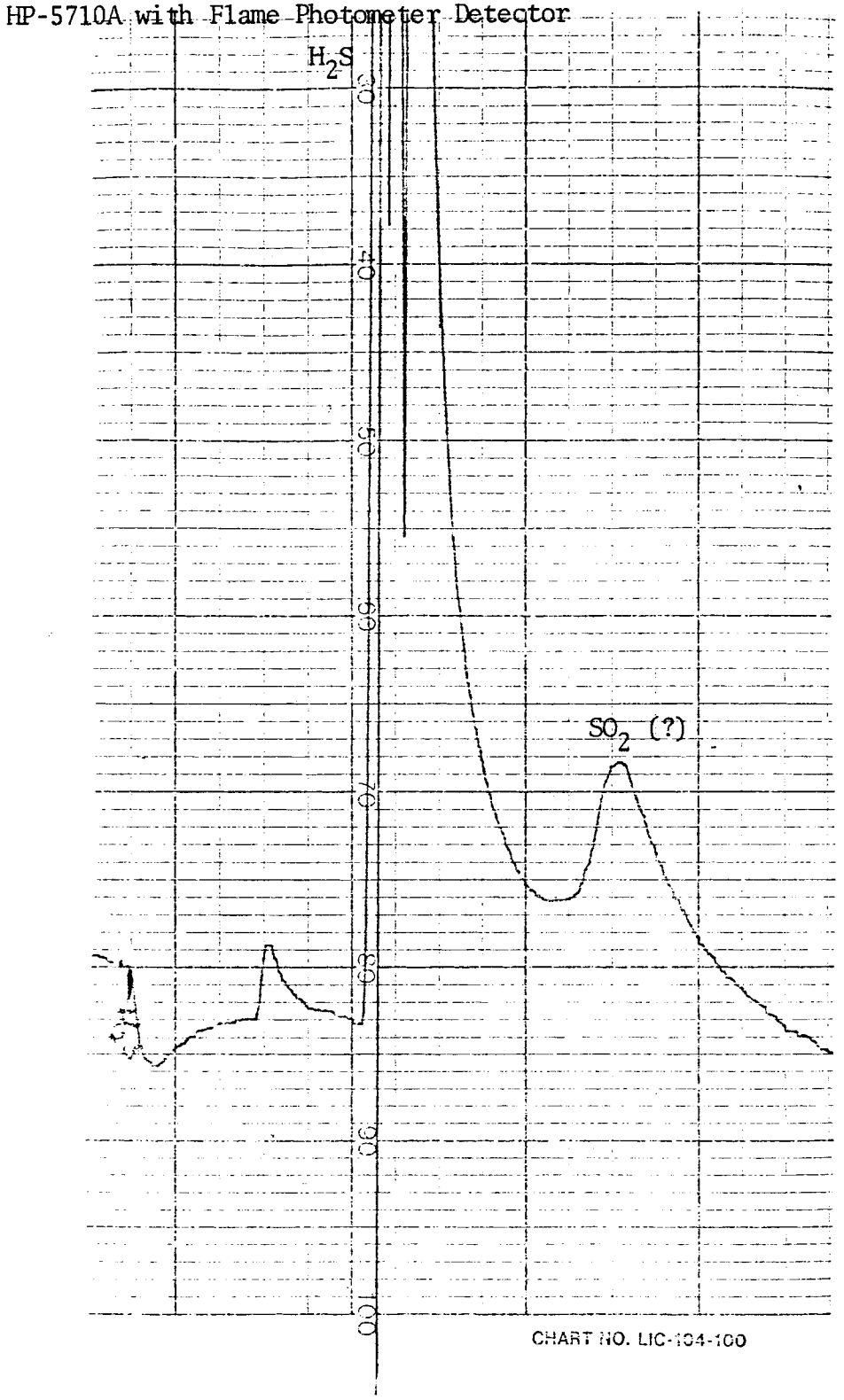

FIGURE 4. Trace of Undigested Untreated Sludge Spiked with H_2S

Frequent checks were made both of the syringe and the bottles to make sure that there was no residual odor from previous samples.

Beginning with samples which had been at ambient temperature only during transit from Sandia and kept frozen in the storage interval at PNL, the routine was repeated each day for a week excepting that no samples were analyzed during the weekend, at Sandia's request. Thus, samples were analyzed on days designated in the text as Days 1, 2, 3, 4, and 7, respectively. Also the original samples A and B (digested, irradiated and digested, unirradiated control, respectively) were found by Sandia to be non-representative and were thus replaced by representative samples. Thus, samples C and D were analyzed at a different time than A and B. Otherwise, all samples were analyzed in an identical fashion.

RESULTS

The actual GC traces obtained are reproduced directly in Appendix B (Figures B-1 to B-39).

An example of an air injection is shown in Figure 5, for illustration purposes. A typical GC trace from an injected sample (B-4 on day 1) is shown in Figure 6. In all GC traces there is a sharp peak shortly after the injection point, caused by air. This is followed by a very large, broad, and tailed negative peak caused by water. There is no way of avoiding this water peak, which is unfortunate, since peak 'A' is superimposed on it, and peak 'B' is on the end of the water recovery portion of the chromatogram. Only peak 'C' is free of water interference. On the air injection chromatogram small peaks and humps are present. These are due partly to the water recovery which is not normally completely symmetrical, and partly to traces of organic contaminants from the syringe (plasticizer degradation products) and from sewage volatiles present in laboratory air.

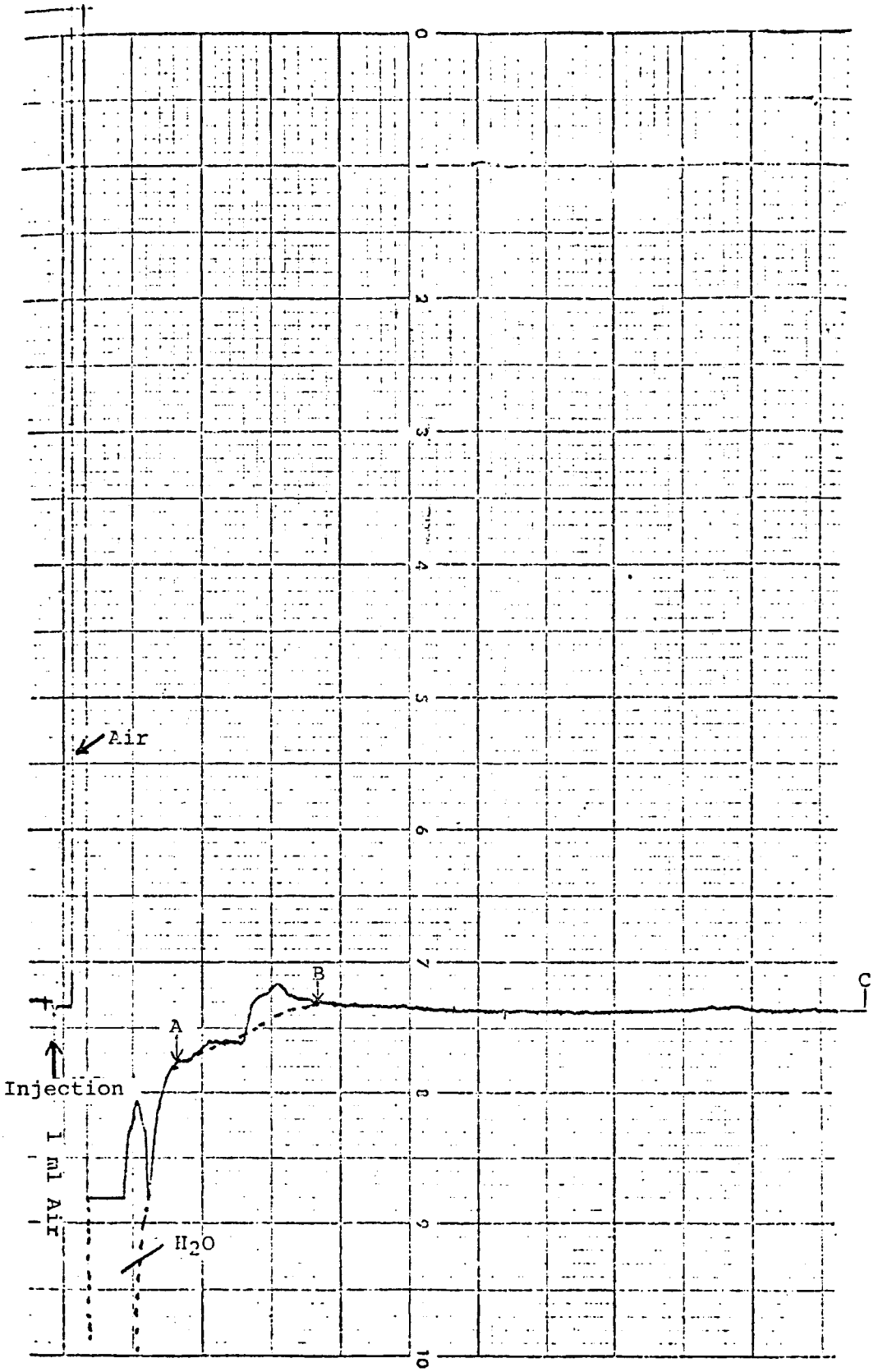

FIGURE 5. Laboratory Air (x40), 1 ml

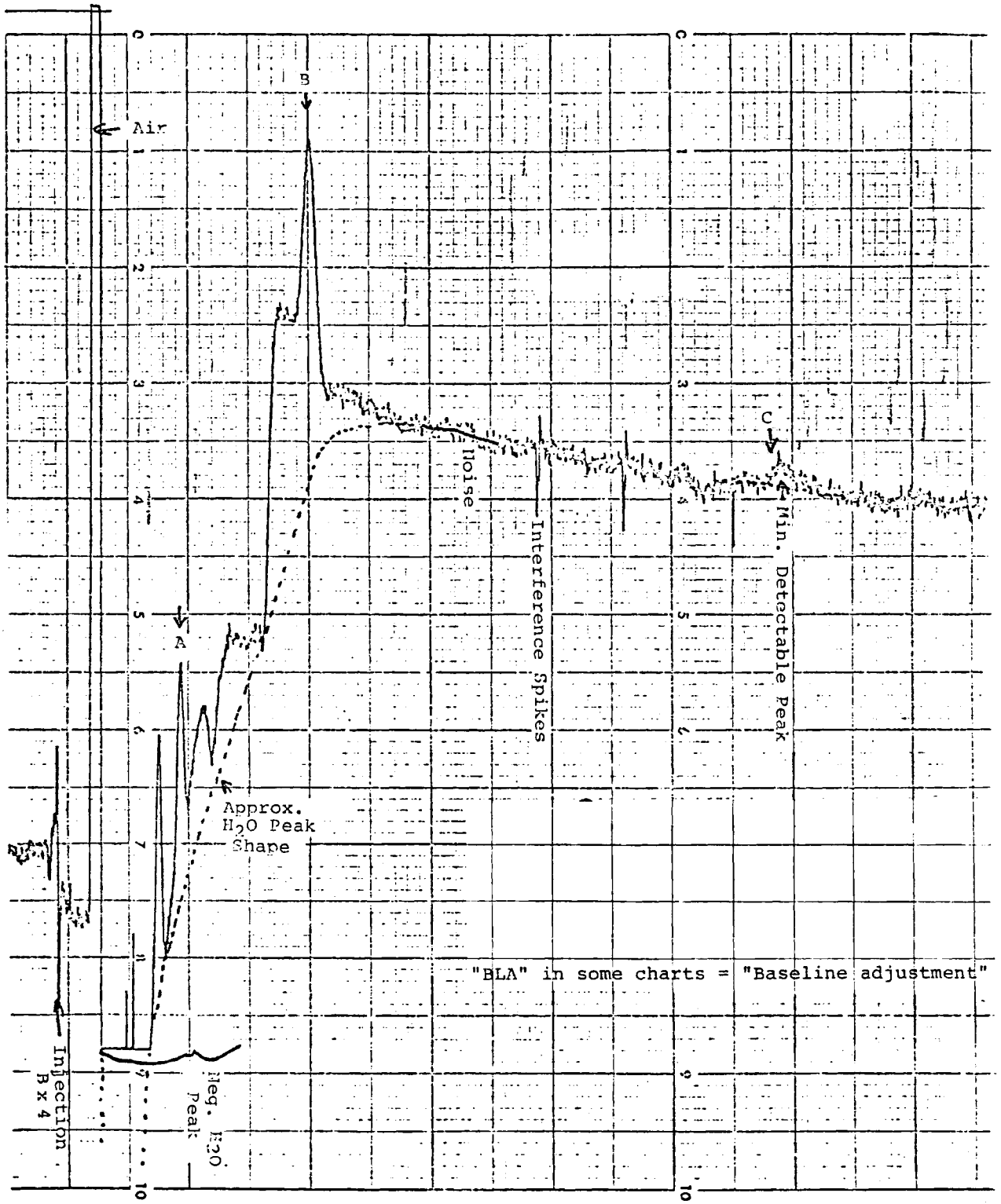

FIGURE 6. Sample B' (Original) to Illustrate Typical GC Trace

Allowance has to be made in any quantitative determination for the presence of these materials and for the fact that a positive component peak can be superimposed on a negative water peak. Together with the fact that on the ECD detector different chemical groups show a different response, these factors combine to make it difficult to obtain quantitative data. In Phase I of this research quantitation was not required; thus, no special precautions were taken. If quantitative results are required for future work, this can best be obtained by either selective removal of water (e.g., on a vented precolumn), by incorporation of an internal standard, or by using an already identified component of the sample as a solvent for the remainder.

Using the ECD detector it should be remembered that the peaks appearing in the chromatogram represent at most a few picograms of organic volatiles. The absence of any contamination at these levels would be an excellent indication of an instrument malfunction.

Samples A and B (digested) were obviously much less odorous than C and D (undigested), on the basis of the odor panel assessment. The GC gave similar results in that peak heights on identical injections were much lower for A and B than for C and D (A and B being the digested samples). In Figure 6 the positions of component peaks A, B, and C have been marked and are seen to be absent in the air injection (Figure 5). The difference in response for peaks 'A', 'B', and 'C' is the cause of there being two sets of GC traces for comparison purposes. A and B sometimes gave measurable peaks only at the higher sensitivity of x4, while C and D frequently gave off-scale peaks at this sensitivity and required analysis at x40 to give on-scale peaks. The x4 chromatograms are considerably noisier than the x40 chromatograms. In fact, some peaks in A and B samples are near the lower detectable limit for this instrument under these conditions. It will be noted from the example GC trace (Figure 6) that there is a very

large water peak, necessitating a baseline adjustment (designated BLA) on some chromatograms. The baseline was adjusted in order that peaks A and B, and any other minor peaks which sometimes were recorded, could be obtained on-scale in the middle of the water peak.

Although a number of peaks were recorded, there were three major components which appeared in every chromatogram. These are the peaks designated A-C. Other peaks have not been labeled. In general, from the retention times, the sensitivity of response on the ECD, and the odors, the compounds which cause peaks on these chromatograms are probably lower members of the thiol, amine, sulfide, nitrile homologous series, or multifunctional compounds containing these groups.

The actual peak heights of peaks A, B, and C are recorded in Table 4, for samples designated A, B, C, and D. These were the sewage samples taken for the odor panel testing in the second week. Note that A, B, and C, D samples were tested during different periods, as noted earlier (p.24). Peak heights are measured at x4 and x40 for samples A and B, and at x40 only for C and D because of the overall greater concentration of components in these samples. The chromatograms from which these measurements were made are attached (Appendix B). It should be stressed again that the data are semi-quantitative; the time and sample variations observed are correct in form, but they may actually vary in magnitude.

From Table 4 and Figures 2-6 the following relationships are apparent:

1. The digested and undigested sewage samples, whether heated and irradiated or not, show different and characteristic time variations of components A, B, and C. Peaks 'A' and 'C' are diminished in the digested, as compared to the undigested, samples. Peak B reaches a maximum on day 2,

TABLE 4. Relative Intensities of GC Peaks A-C in Digested Irradiated and Digested Control Sewage Samples over a One-Week Period

Sample A	Digested Treated (x4)			Digested Treated (x40)		
	A	B	C	A	B	C
Day 1	0.3	>8	0.25	0	2.5	0
Day 2	2	>11	0.5	0.1	>11	0.1
Day 3	0.1	>6	1.2	0.3	1.3	0.1
Day 4	0	0.3	0.3	0	0	0
Day 7	0	0.4	0	0	0	0

Sample B	Digested Untreated (x4)			Digested Untreated (x40)		
	A	B	C	A	B	C
Day 1	1	>5	0.1	0.1	1.5	0
Day 2	0	>8	3	0.1	>11	0.1
Day 3	0	>4	1	0.3	2	0.1
Day 4	0	0.2	0	0	0	0
Day 7	0	0.4	0	0	0	0

Sample C	Undigested Treated (x40)		
	A	B	C
Day 1	3.0	5.4	0.5
Day 2	2.45	6.7	0.9
Day 3	4.6	8.5[c]	0.55
Day 4	2.9	8.3[c]	0.3
Day 7	3.0	6.2	0.2

Sample D	Undigested Untreated (x40)		
	A	B	C
Day 1	4.7	6.3	0.2
Day 2	6.3	6.0	0.6
Day 3	5.7	6.1	0.3
Day 4	4.6	8.4[c]	0.6
Day 7	3.4	6.1	0.5

c - calculated (off-scale peak)

somewhat greater in samples A, B than in C, D.

2. There is a distinct maximum intensity in each of the components A-C, in all samples, although the time of occurrence and intensity of this maximum vary.

3. Irradiation and heat treatment had little effect on the intensity of peaks A-C, relative to the respective controls.

VOLATILE EFFLUENT TRAPPING

One major advantage of the ECD for this work is that it is non-destructive of the sample. Whereas flame ionization and flame photometry detectors burn the sample in a hydrogen flame, ECD and hot wire detectors depend on the detection of differences in physical properties between the carrier gas and organic components.

Although not a specific requirement for this research, the collection of GC peak effluents and subsequent testing by odor panel experts would be a major part of any subsequent research. Thus, it was felt that an attempt at collection would be justified. Consequently, peaks A, B, and C were collected from one sample, using separate disposable syringes placed in the ECD effluent tube. Four members of the odor testing panel were then asked to smell the contents of the syringes. Of the three peaks only 'B' was detected by all four; A and C were below the detectable threshold. However, the ability to detect B proved that the collection of individual GC peaks for testing is a workable approach.

To confirm that peak 'B' was indeed collected and tested, a repeat collection was performed. Instead of subjecting the sample to an odor panel test, it was reinjected into the GC. The appearance of a peak in the normal position for 'B' proved that this was indeed the trapped component.

CONCLUSIONS

From the above results and discussion, the following conclusions were reached:

1. Detection of sewage volatiles is practicable by GC using an ECD but not using a flame ionization detector.
2. There were gross differences between digested and undigested samples, as shown by GC results.
3. There were small but not gross differences between heated/irradiated and untreated samples.
4. Collection of individual GC peaks for odor testing is possible.
5. All components of sewage volatiles detected showed a time variation with a distinct maximum after air exposures of 2-4 days.
6. Hydrogen sulfide was identified as one sewage odor component.
7. The objectives pertaining to chemical identification and monitoring of sewage samples specified for this research were achieved and, in some cases, exceeded.

COMPARISON OF ODOR PANEL DATA AND CHEMICAL ANALYSES

It should not be assumed that a particular compound has the greatest influence on sewage odor just because the GC analysis maximum peak height of that compound occurred at the same point in time as the odor panel observed the strongest odor. Effects of individual components of a mixture are rarely additive. They are more often synergistic. Odorants of similar characteristics, when mixed, may produce odor intensities that are greater than the intensity of any of the pure odorants.[a]

Even components that are too dilute to be measured on the GC may influence the odor of the sewage. However, comparison of the odor panel work and the GC traces of the sewage sludge to illustrate when a trend may be developing or to use as a guide for future work are valid.

Although results of the GC analyses of sewage samples are not quantitative, treated undigested sewage contained somewhat more of the volatile components than untreated undigested sewage. Threshold odor numbers (T.O.N.) for treated undigested sewage were also higher (stronger odor) than the T.O.N.'s for the untreated undigested sewage.

The maximum T.O.N. of untreated undigested sewage sludge for Replication II (the replication which was used for the GC analysis) occurred on day 4 (237,000). This is also the point when peak B of the three peaks identified in the GC traces reached its maximum intensity (see Tables 2 and 4).

In a similar manner the maximum T.O.N. for treated undigested sewage sludge occurred on day 4 (683,000). Peak B was at its maximum on days 3-4 for the GC trace of treated undigested sewage.

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a. D. T. Hill and C. L. Barth, "Quantitative Prediction of Odor Intensity," Transactions of the ASAE, vol. 19, no. 5, American Society of Agricultural Engineers, 1976.

As noted in the section on Chemical Analysis, peak B was collected from one sample and the odor of peak B was detectable.

The previous results suggest that peak B has some influence on the odor of the undigested sewage sludge; however, that is all that can be stated. There is no indication of the degree of influence that peak B exerts on the odor of the undigested sludge. Additional work would be necessary to determine if an increase in peak B always corresponded to an increase in the odor of the undigested sewage.

For digested sewage sludge, peak B occurred in a greater concentration in the treated sludge than in the untreated sludge. Also the T.O.N.'s for treated digested sewage sludge were much greater than the T.O.N.'s for untreated sludge (Table 3). However, the digested sewage sludge did not seem to exhibit the same pattern as the undigested sludge, i.e., maximum height of peak B at the same time as the maximum T.O.N.

The maximum T.O.N. for untreated digested sewage sludge occurred around the third and fourth days for Replication I. Peak B reached its maximum on day 2. The intensity of all three peaks (A-C) identified in the GC analysis had decreased by the fourth day (Tables 3 and 4). Thus, it does not appear as if any of the three peaks--A, B, or C--could be used as a method for directly indicating the odor of untreated digested sewage sludge.

The maximum T.O.N. for treated digested sewage sludge occurred on day 3 for both Replications I and II. At this point in time both peaks A and B were decreasing on the GC traces. However, peak C did increase on day 3 for the treated digested sewage sludge.

It appears that the three components identified in the GC analysis do have an influence on the odor of sewage sludge. Peak B might be useful in determining the odor strength of

undigested sewage sludge. Perhaps a large peak B on the GC analyses would indicate strong odor. However, as previously stated, no conclusions can be drawn on the degree of influence that peaks A-C exert on the odor of the sewage sludge studied and further investigation would be necessary in order to draw any concrete conclusions.

APPENDICES

APPENDIX A

TABLE A-1. Individual Judges' Scores[a] for Undigested Treated Sewage Sludge Samples

Judge	Replication II					Replication III				
	Day					Day				
	1	2	3	4	7	1	2	3	4	7
1	>70	240	>350	700	240	240	140	200	100	140
2	>70	240	350	700	240	100	350	240	140	140
3	>70	240	350	700	200	240	200	<200	200	140
4	>70	240	350	1,000	240	240	240	200	140	140
5	>70	240	350	500	200	70	350	200	100	140
6	>70	100	350	500	200	70	350	200	200	140

a. Scores listed in thousands, e.g., Replication II, Judge 1, Day 1 - 70 = 70,000

TABLE A-2. Individual Judges' Scores[a] for Undigested Control Sewage Sludge Samples

Judge	Replication II - Day					Replication III - Day				
	1	2	3	4	7	1	2	3	4	7
1	35	200	100	200	140	70	200	70	200	70
2	35	70	240	240	200	70	50	100	70	70
3	50	100	200	140	200	20	14	100	240	70
4	70	200	140	140	140	70	70	140	200	70
5	35	100	200	350	240	50	100	200	140	50
6	20	100	70	350	240	24	100	100	140	140

a. Scores listed in thousands, e.g., Replication II, Judge I, Day 1 - 35 = 35,000

TABLE A-3. Individual Judges' Scores[a] for Digested Treated Sewage Sludge

Judge	Replication I - Day					Replication II - Day				
	1	2	3	4	7	1	2	3	4	7
1	24	>200	350	240	>140	50	500	<350	240	>200
2	35	>200	500	200	>140	50	240	350	350	>200
3	10	100	350	200	140	50	240	500	240	140
4	50	>200	1,000	200	>140	50	500	500	200	>200
5	24	>200	1,400	240	>140	50	500	700	200	>200
6	50	>200	500	200	>140	35	500	350	200	200

a. Scores listed in thousands, e.g., Replication II, Judge 1, Day 1 - 24 = 24,000

TABLE A-4. Individual Judges' Scores[a] for Digested Control Sewage Sludge

Judge	- - Replication I - - Day					- - Replication II - - Day				
	1	2	3	4	7	1	2	3	4	7
1	24	100	100	200	100	10	200	70	100	>200
2	10	100	140	200	70	50	70	70	50	>200
3	10	100	70	100	70	50	70	70	200	140
4	35	50	240	200	100	50	200	70	200	>200
5	10	50	240	200	70	50	70	240	200	>200
6	35	35	240	200	100	24	100	70	100	>200

a. Scores listed in thousands, e.g., Replication I, Judge 1, Day 1 - 24 = 24,000

TABLE A-5. Results[a] of Statistical Analysis of T.O.N.[b] of Undigested Treated Sewage Sludge

Replication II[c]					Replication III				
99% Confidence Level									
Day					Day				
1	2	3	4	7	1	2	3	4	7
70	217	350	683	220	160	272	207	147	140
95% Confidence Level									
Day					Day				
1	2	3	4	7	1	2	3	4	7
70	217	350	683	220	160	272	207	147	140

a. Means underlined are significantly different.
b. T.O.N.'s are listed in thousands, i.e., 70 = 70,000.
c. Data from Replication I were not analyzed as judges could detect odor in all the samples.

TABLE A-6. Results[a] of Statistical Analysis of T.O.N.[b] of Undigested Untreated Sewage Sludge

Replication II[c]					Replication III				
99% Confidence Level									
Day					Day				
1	2	3	4	7	1	2	3	4	7
41	128	158	237	193	51	89	118	165	78
95% Confidence Level									
Day					Day				
1	2	3	4	7	1	2	3	4	7
41	128	158	237	193	51	89	118	165	78

a. Means underlined are significantly different.
b. T.O.N.'s are listed in thousands, i.e., 41 = 41,000.
c. Data from Replication I were not analyzed as judges could detect odor in all the samples.

TABLE A-7. Results[a] of Statistical Analysis of T.O.N.[b] of Digested Treated Sewage

Replication I					Replication II				
99% Confidence Level									
Day					Day				
1	2	3	4	7	1	2	3	4	7
32	183	683	213	140	47	413	458	238	190
95% Confidence Level									
Day					Day				
1	2	3	4	7	1	2	3	4	7
32	183	683	213	140	47	413	458	238	190

a. Means underlined are significantly different.
b. T.O.N.'s are listed in thousands, i.e., 32 = 32,000.

TABLE A-8. Results[a] of Statistical Analysis of T.O.N.[b] of Digested Untreated Sewage

Replication I					Replication II				
99% Confidence Level									
Day					Day				
1	2	3	4	7	1	2	3	4	7
21	72	172	183	85	39	118	98	142	190
95% Confidence Level									
Day					Day				
1	2	3	4	7	1	2	3	4	7
20	72	172	183	85	39	118	98	142	190

a. Means underlined are significantly different.
b. T.O.N.'s are listed in thousands, i.e., 20 = 20,000.

APPENDIX B: GC TRACES

Figures B-1 - B-39

Conditions

Perkin-Elmer 900A chromatograph, operated isothermally at 50°C; 9 ft x ¼ in. glass column containing 3% SE-30 on Chromosorb (80-100 mesh); 30 ml/min of 5% CH_4 in Ar through column; 30 ml/min by-pass flow. Injector 160°C; detector (ECD with ^3H-impregnated foil) 105°C; manifold 200°C.

Samples: 0.5 ml head-space vapor at attenuation x4; 1.0 ml head-space vapor at attenuation x40 (less sensitive than x4).

Samples

*A - Digested, Heat and Radiation Treated

*B - Digested, Untreated Control

C - Undigested, Heat and Radiation Treated

D - Undigested, Untreated Control

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* A and B were run at a later period than C and D since the original samples A and B (not reported here) were found by Sandia to be non-representative.

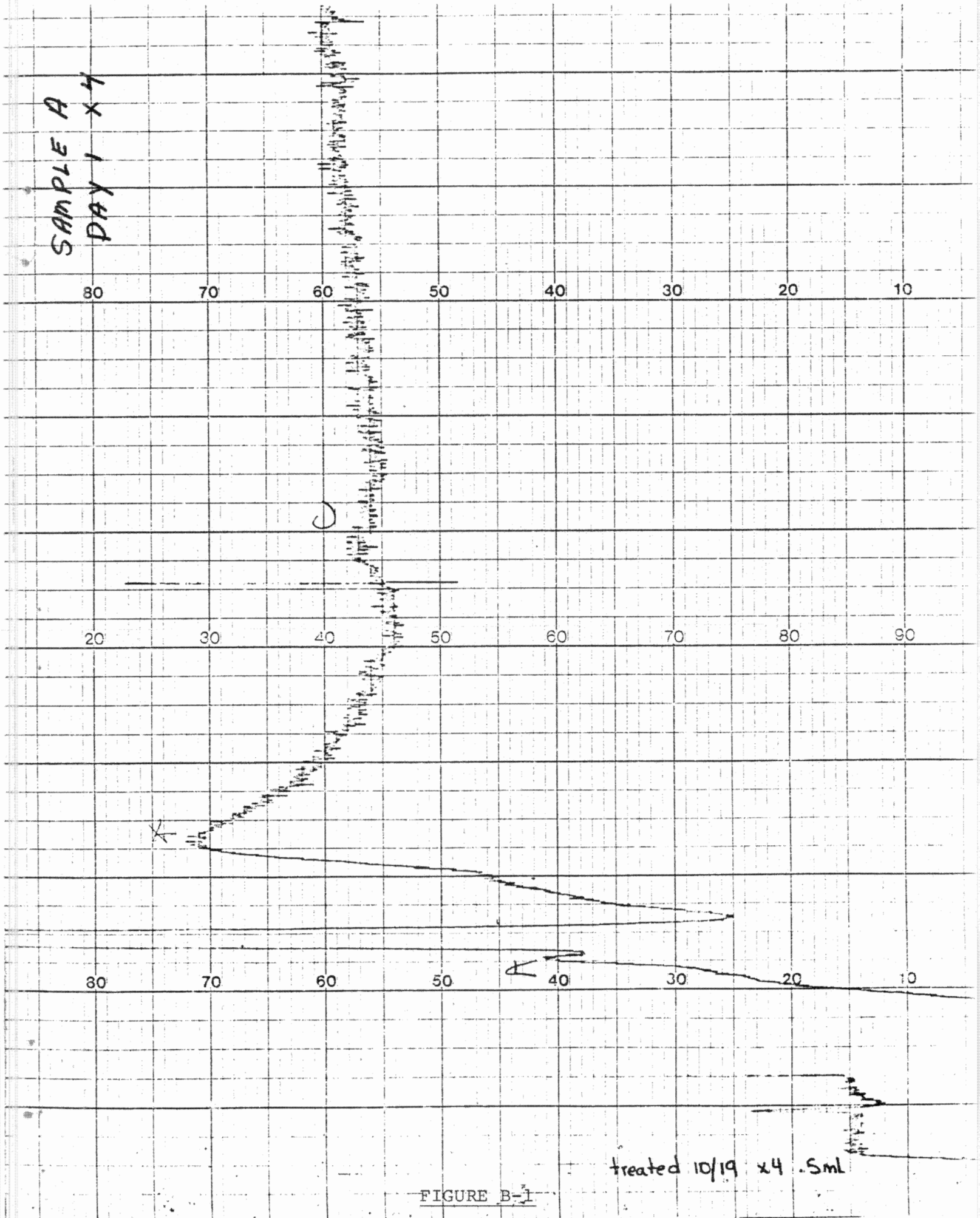

SAMPLE A
DAY 1 x4
80 70 60 50 40 30 20 10
20 30 40 50 60 70 80 90
80 70 60 50 40 30 20 10
treated 10/19 x4 .5ml

FIGURE B-1

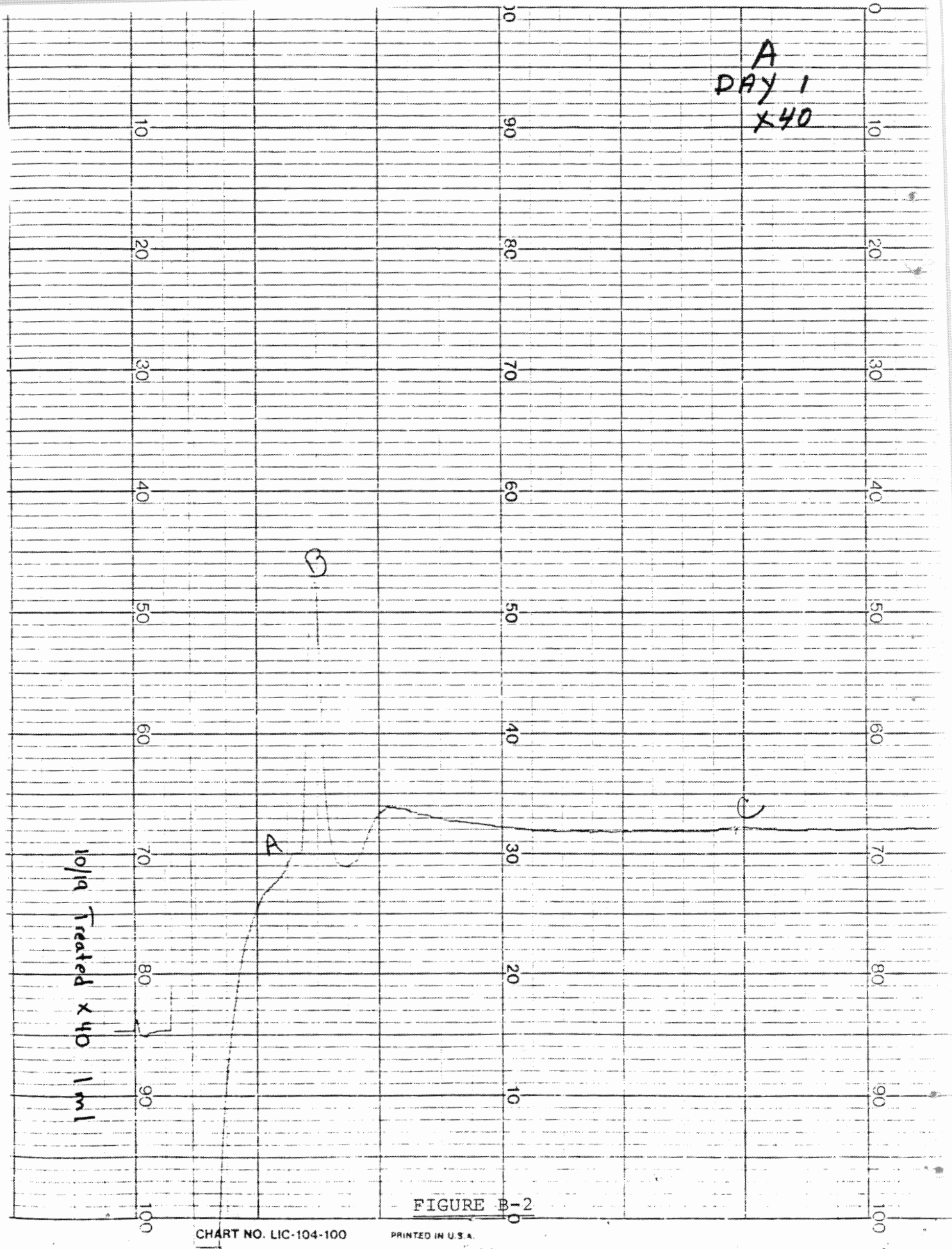


FIGURE B-2

CHART NO. LIC-104-100 PRINTED IN U.S.A.

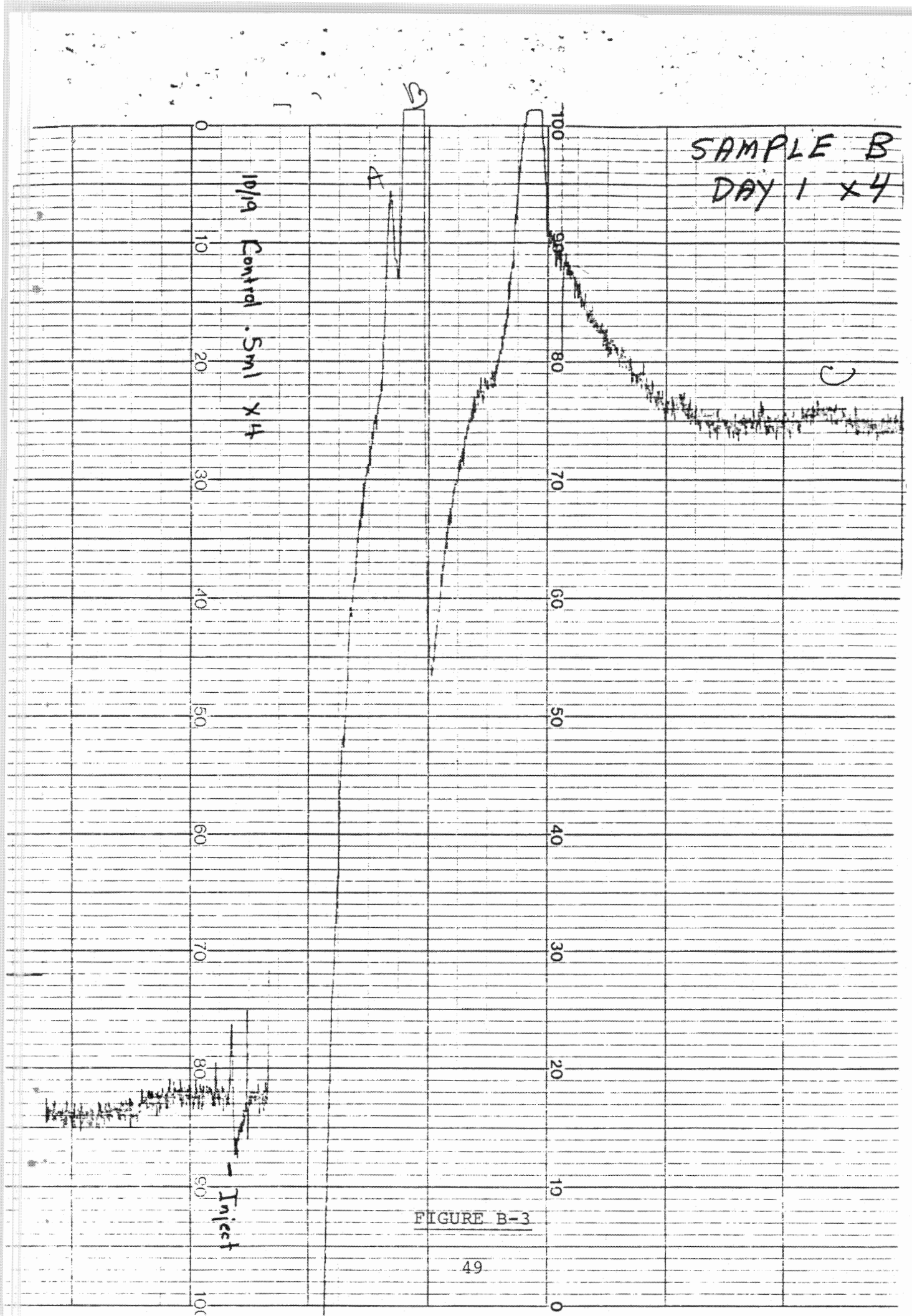

SAMPLE B
DAY 1 x4
10/19 Control .5ml x4
A
B
C
Inject
0
10
20
30
40
50
60
70
80
90
100
100
90
80
70
60
50
40
30
20
10
0

FIGURE B-3

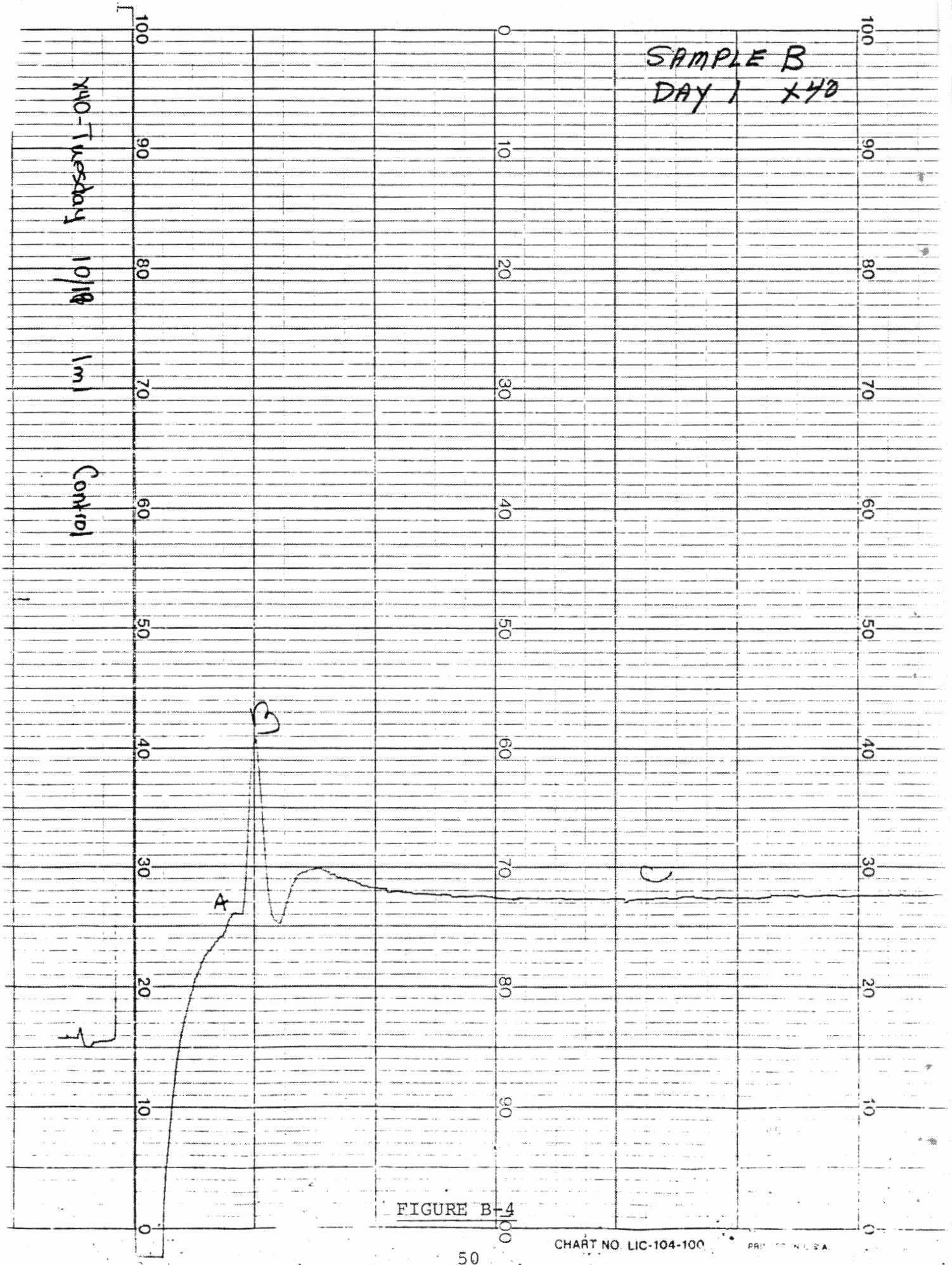


FIGURE B-4

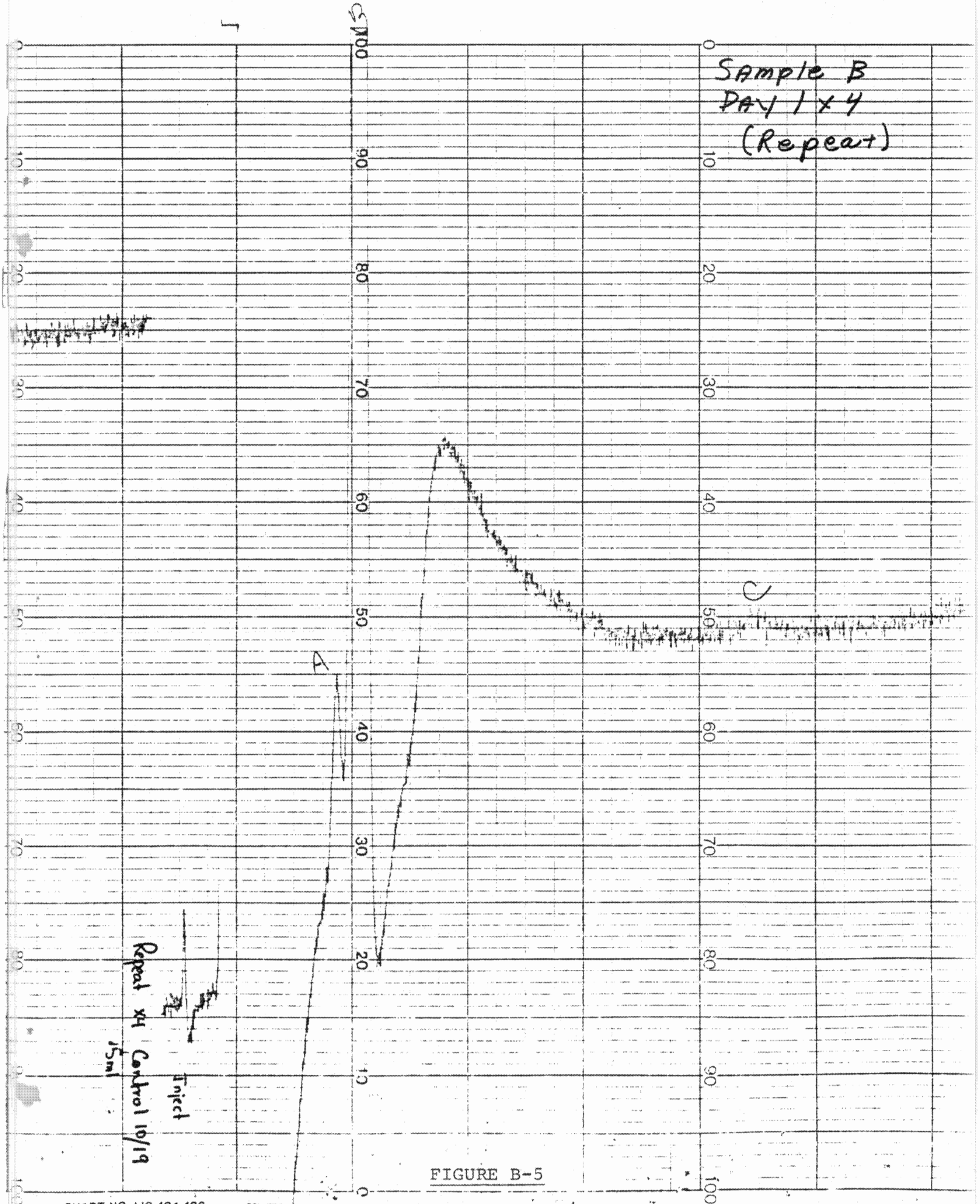
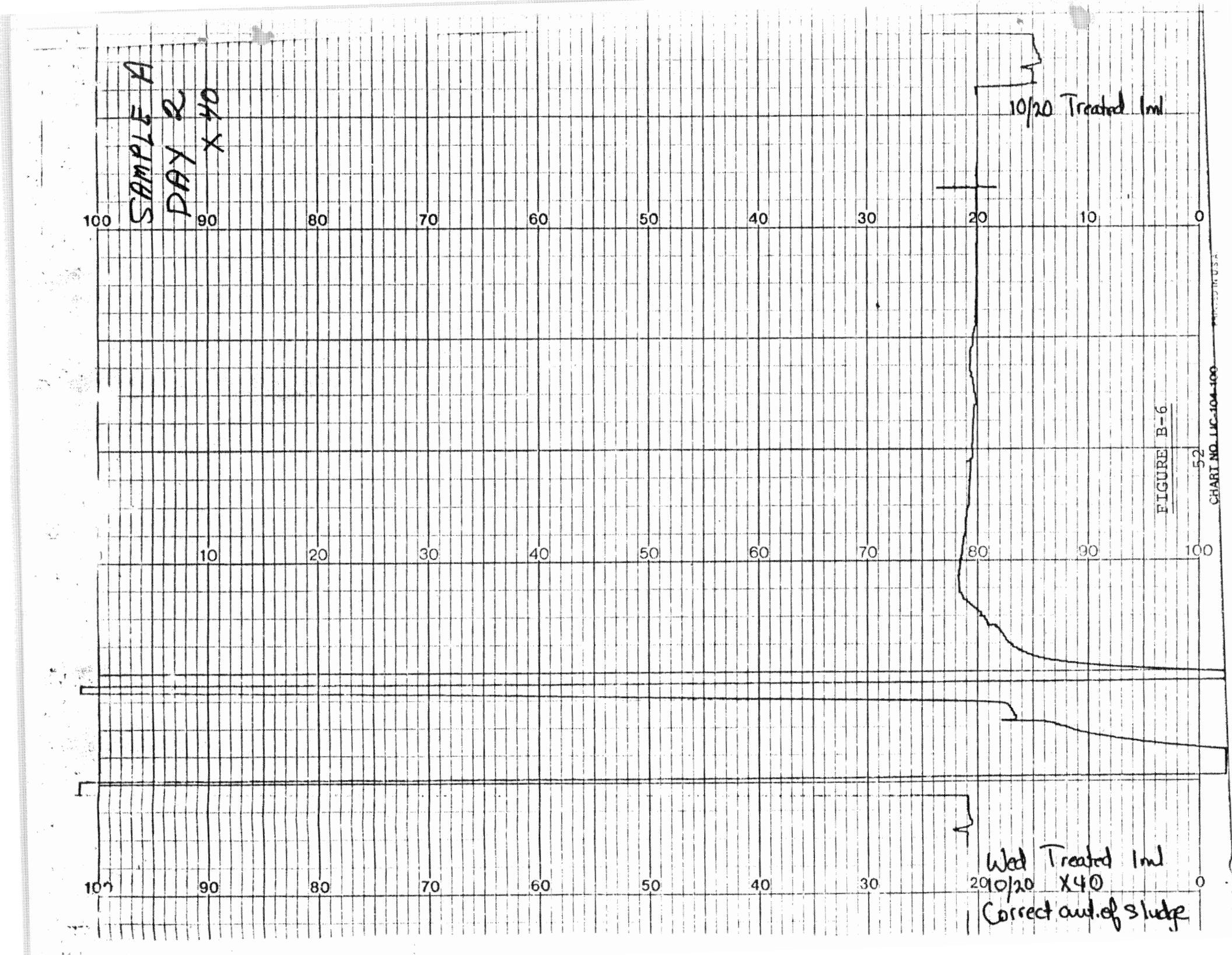

Sample B
Day 1 x 4
(Repeat)
A
C
Repeat x4 Control 10/19
Inject
15ml
CHART NO. LIC-104-100
PRINTED IN U.S.A.

FIGURE B-5


SAMPLE A
DAY 2
X 40
10/20 Treated Inl
100 90 80 70 60 50 40 30 20 10 0
10 20 30 40 50 60 70 80 90 100
Wed Treated Inl
10/20 X40
Correct amt. of sludge
FIGURE B-6
CHART NO. LIC-104-100

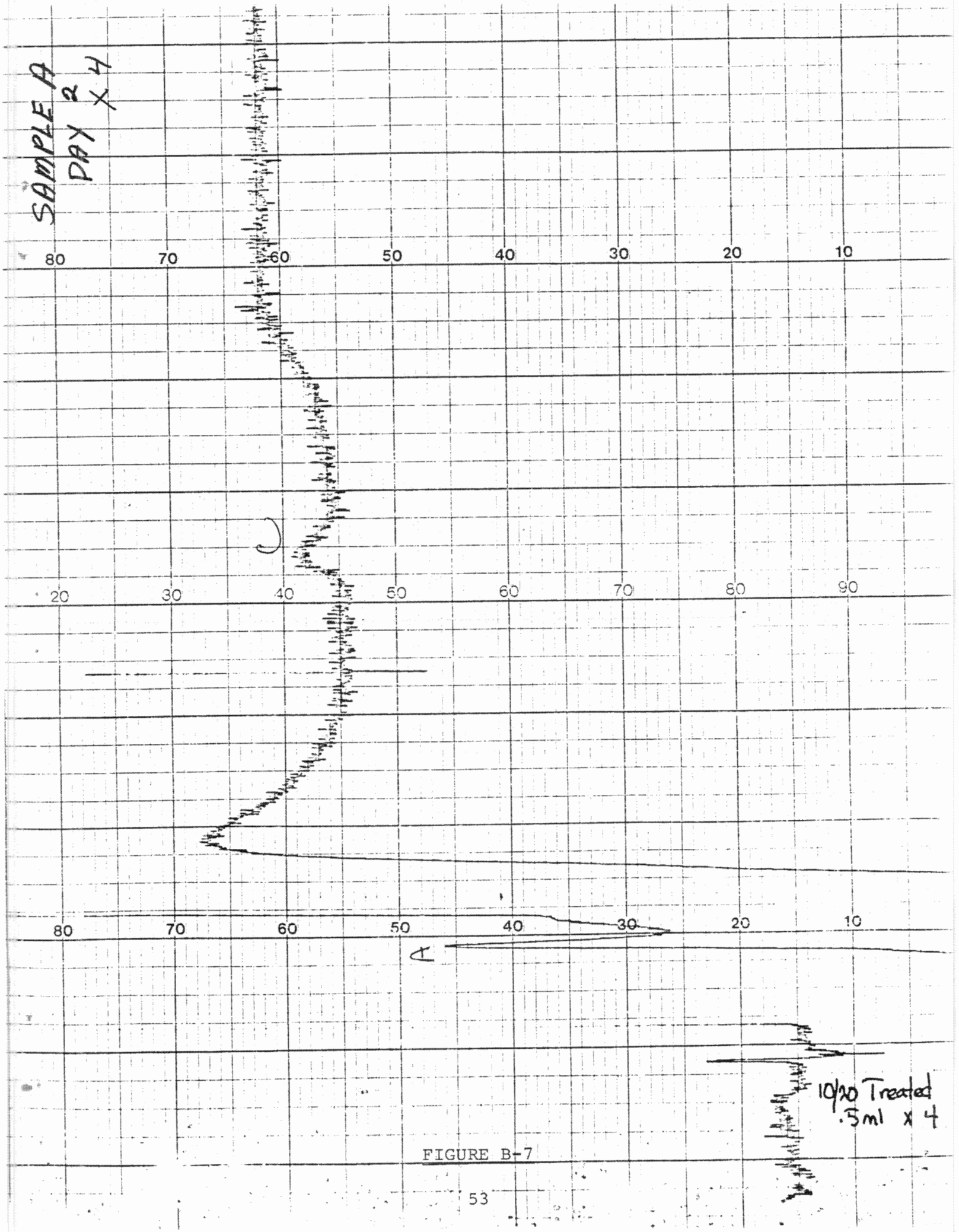

SAMPLE A
DAY 2 x 4
80 70 60 50 40 30 20 10
20 30 40 50 60 70 80 90
80 70 60 50 40 30 20 10
10/20 Treated
.5ml x 4

FIGURE B-7

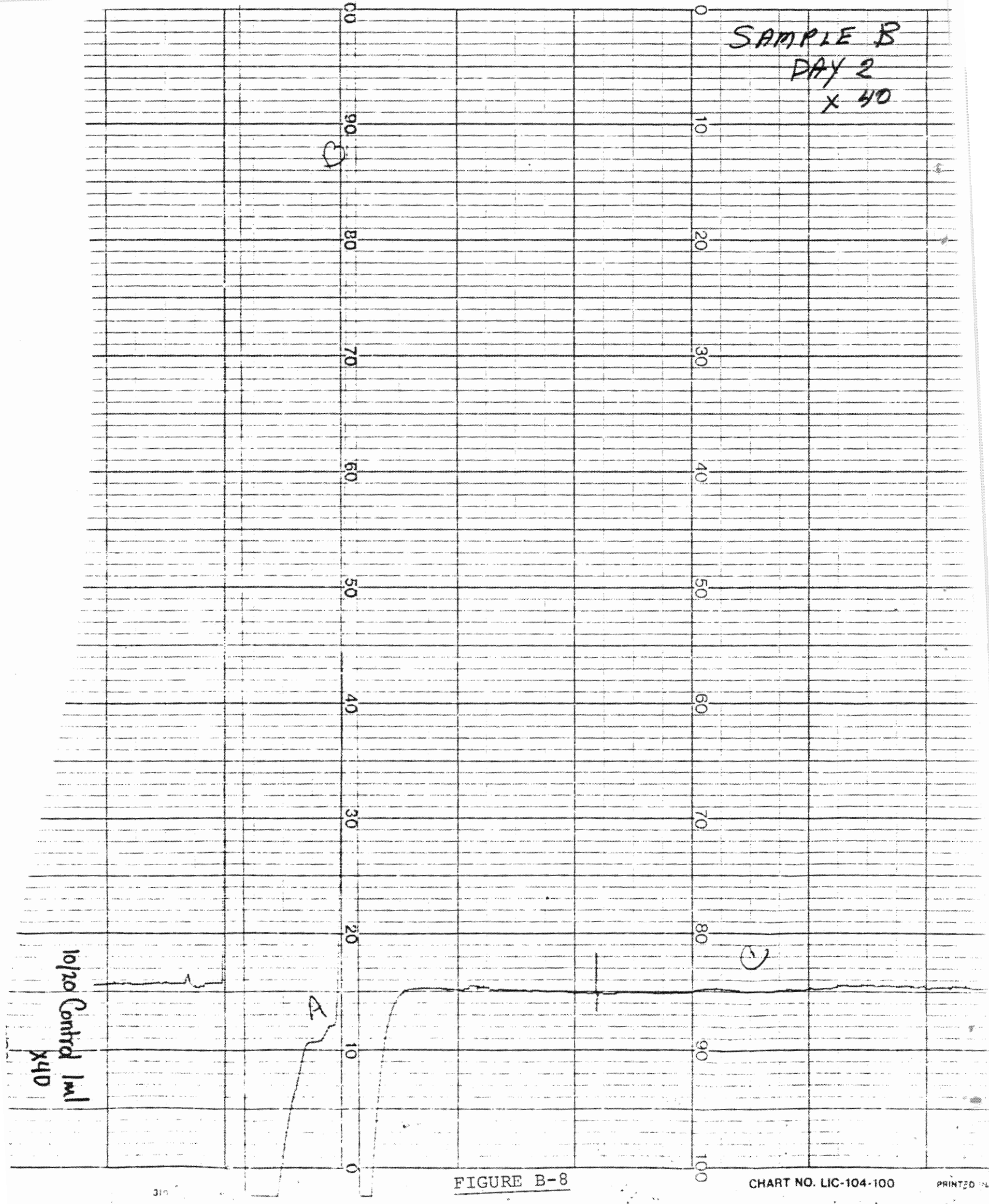


FIGURE B-8

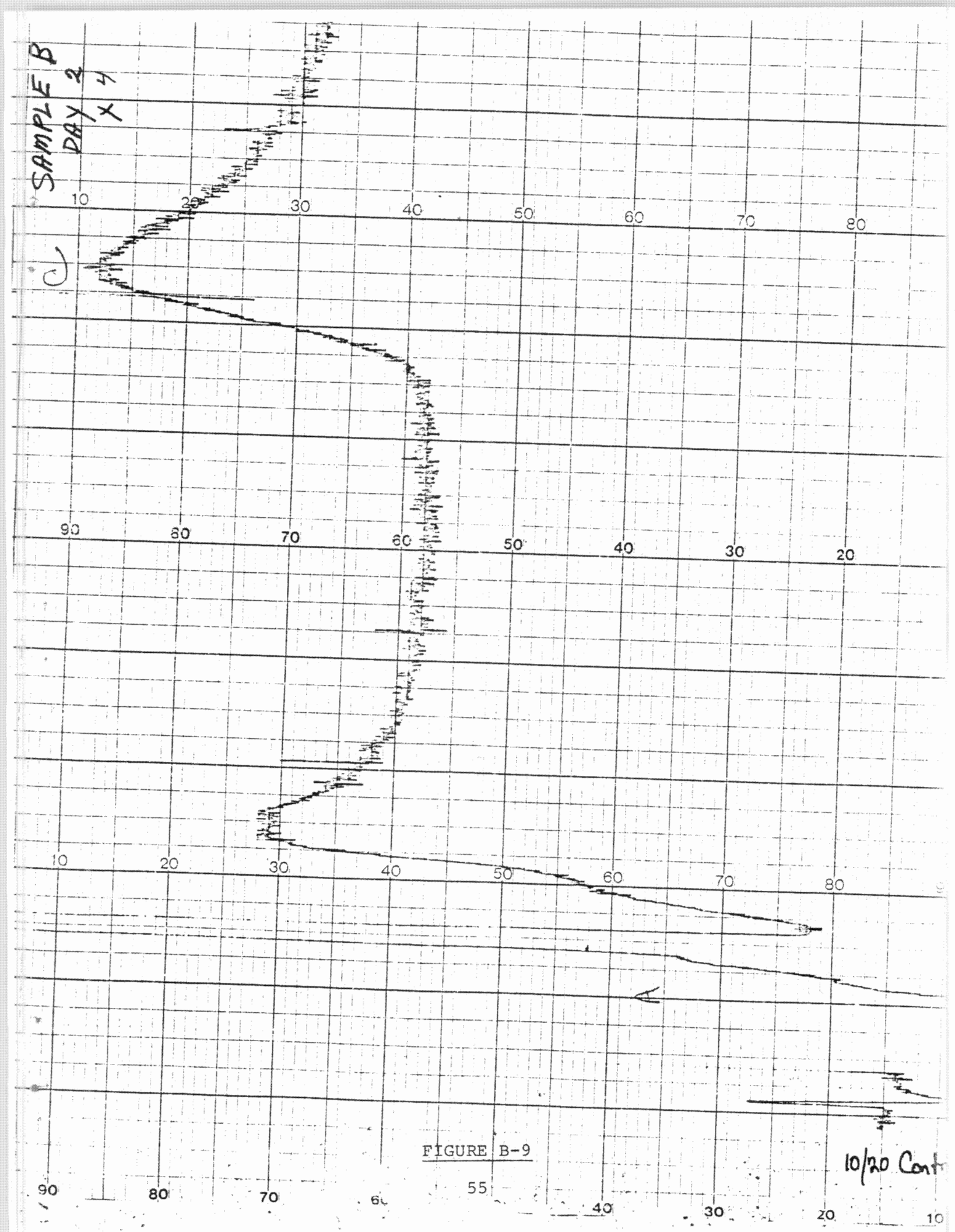

SAMPLE B
DAY 2
X 4
10
20
30
40
50
60
70
80
90
80
70
60
50
40
30
20
10
20
30
40
50
60
70
80
90
80
70
60
40
30
20
10
10/20 Cont

FIGURE B-9

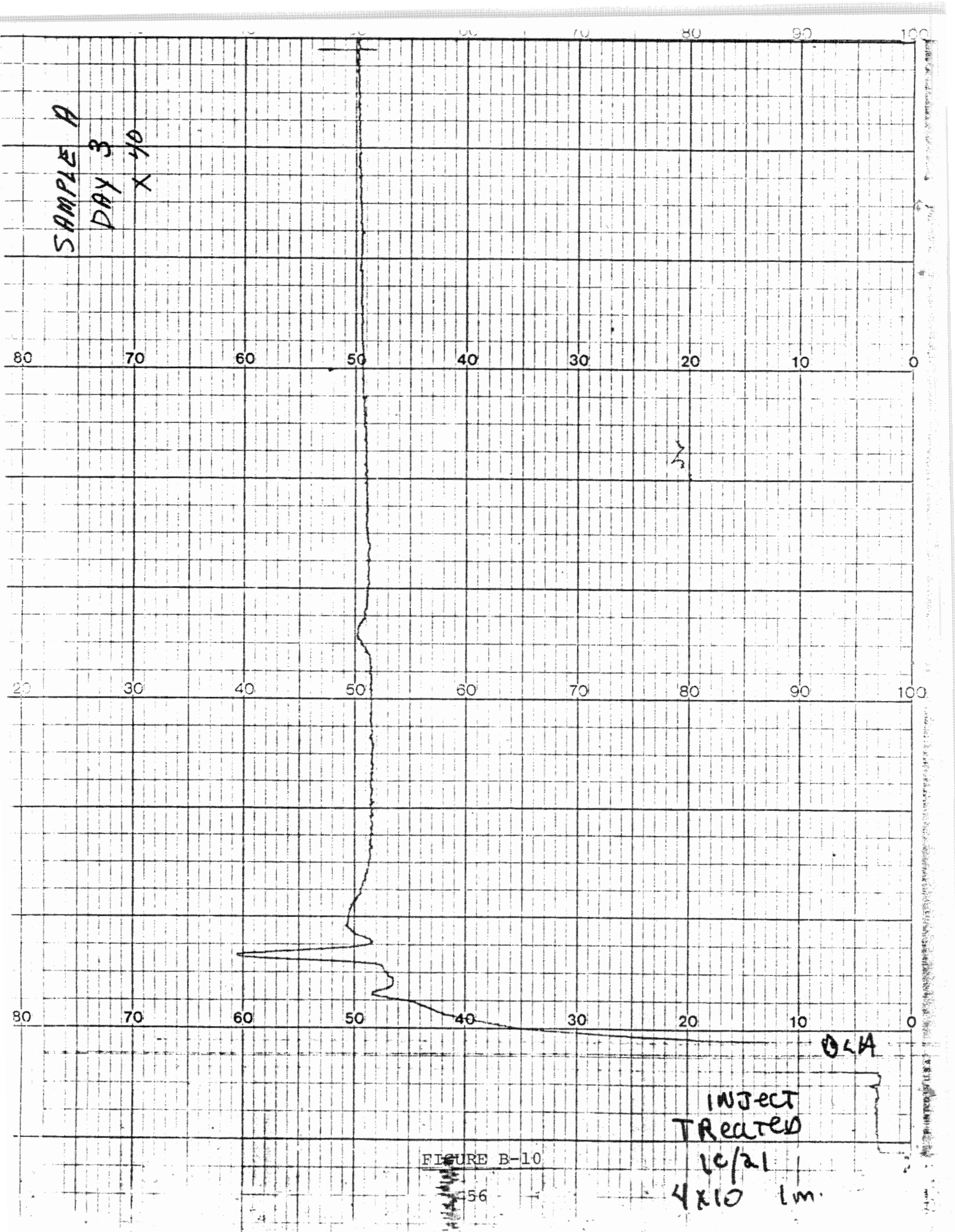

SAMPLE A
DAY 3
X 1/10
80 70 60 50 40 30 20 10 0
20 30 40 50 60 70 80 90 100
80 70 60 50 40 30 20 10 0
BLK
INJECT
TREATED
10/21
4x10 1m.

FIGURE B-10

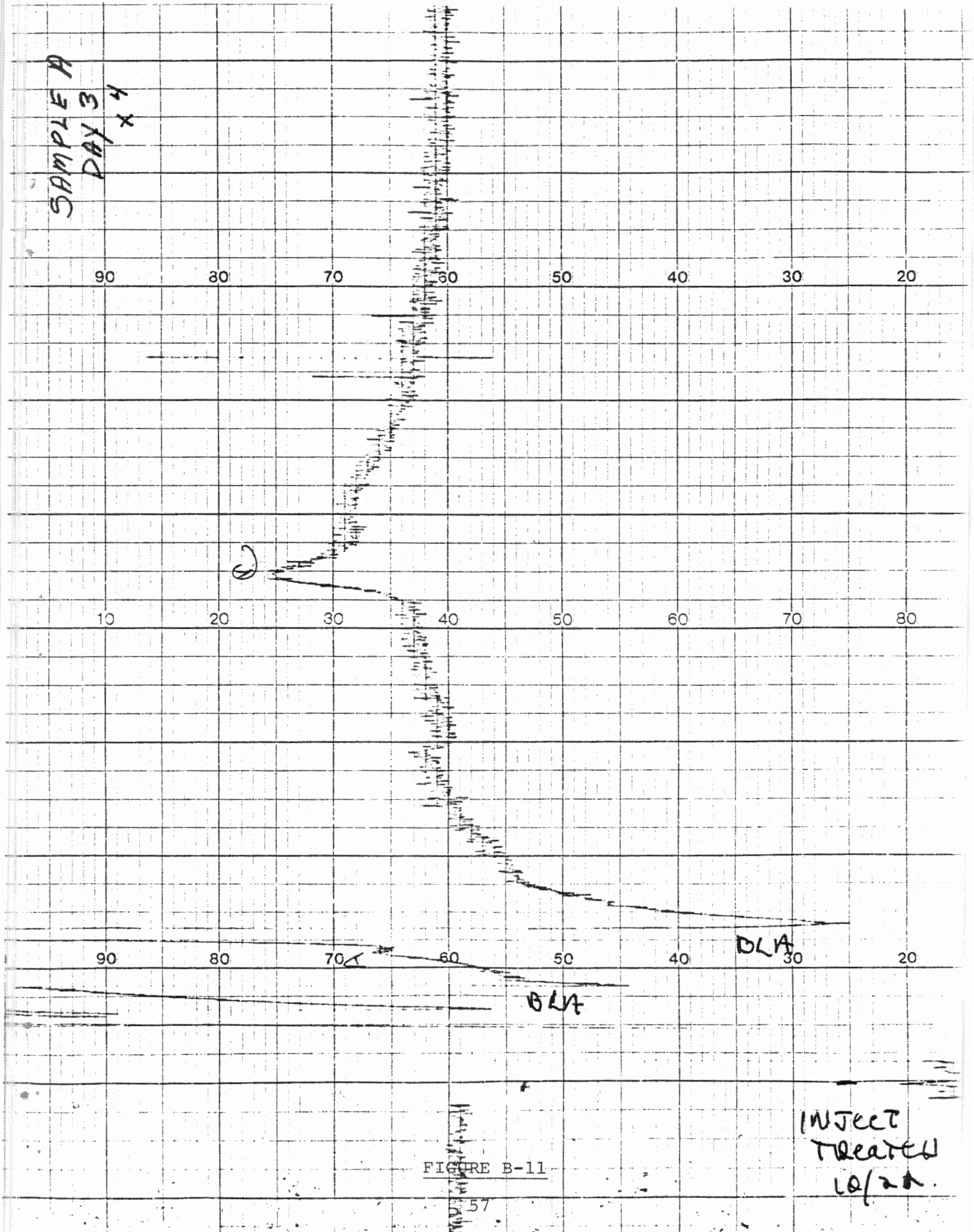

SAMPLE A
DAY 3
x4
90
80
70
60
50
40
30
20
10
20
30
40
50
60
70
80
DLA
DLA
INJECT
TREATED
10/20

FIGURE B-11

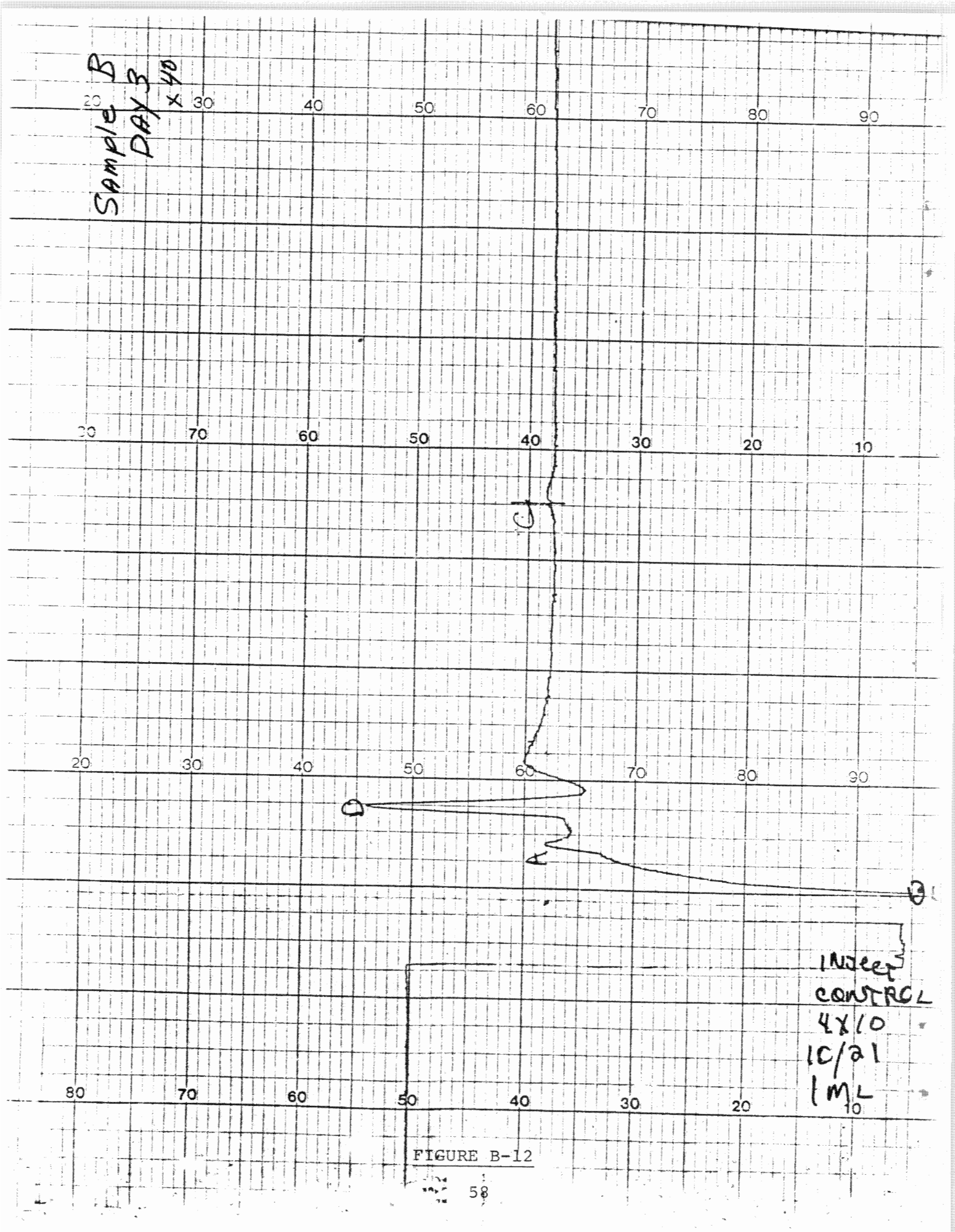

Sample B
DAY 3
x 40
20 30 40 50 60 70 80 90
90 80 70 60 50 40 30 20 10
20 30 40 50 60 70 80 90
80 70 60 50 40 30 20 10
INJECT
CONTROL
4X10
1C/21
1 ML

FIGURE B-12

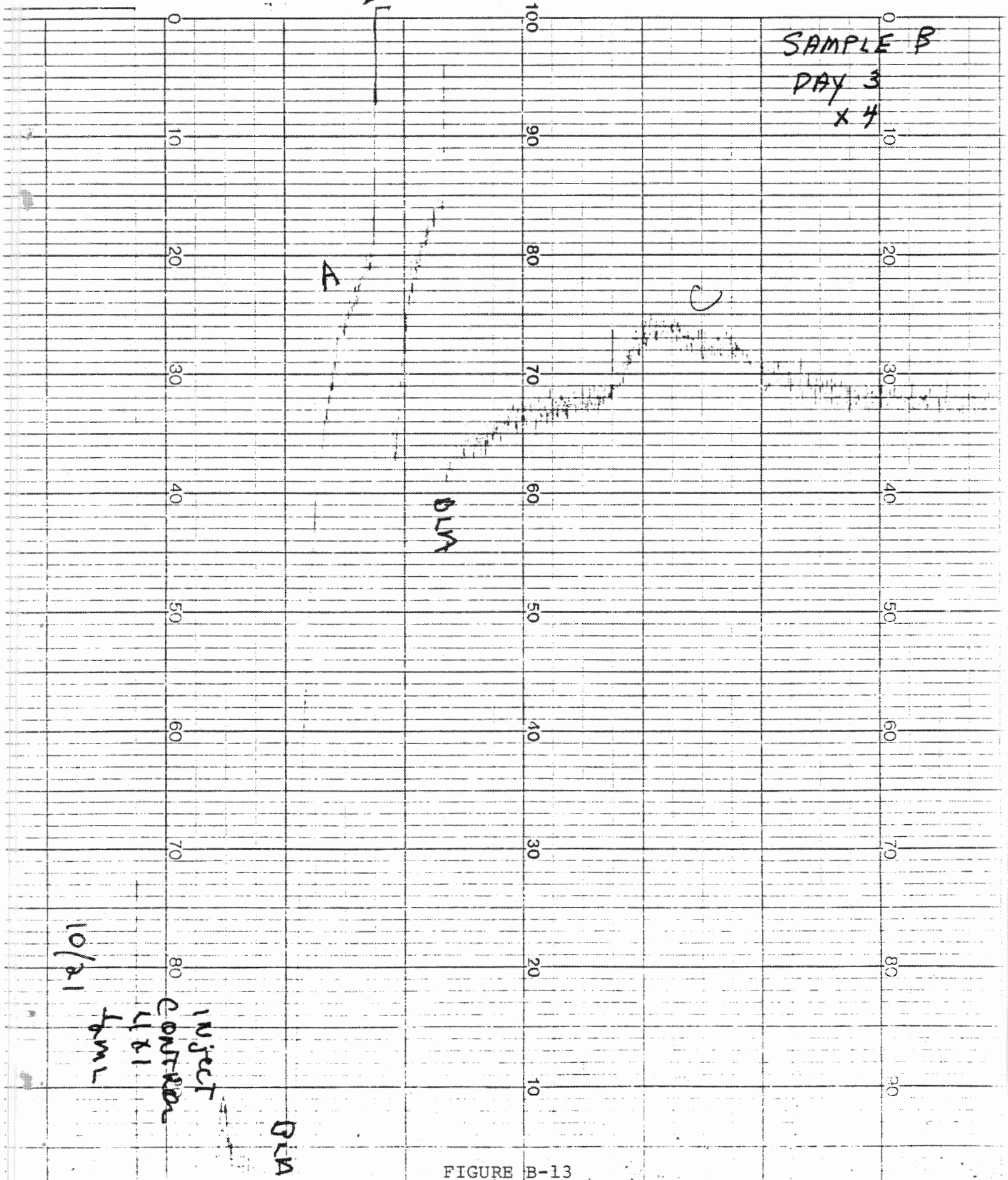


FIGURE B-13

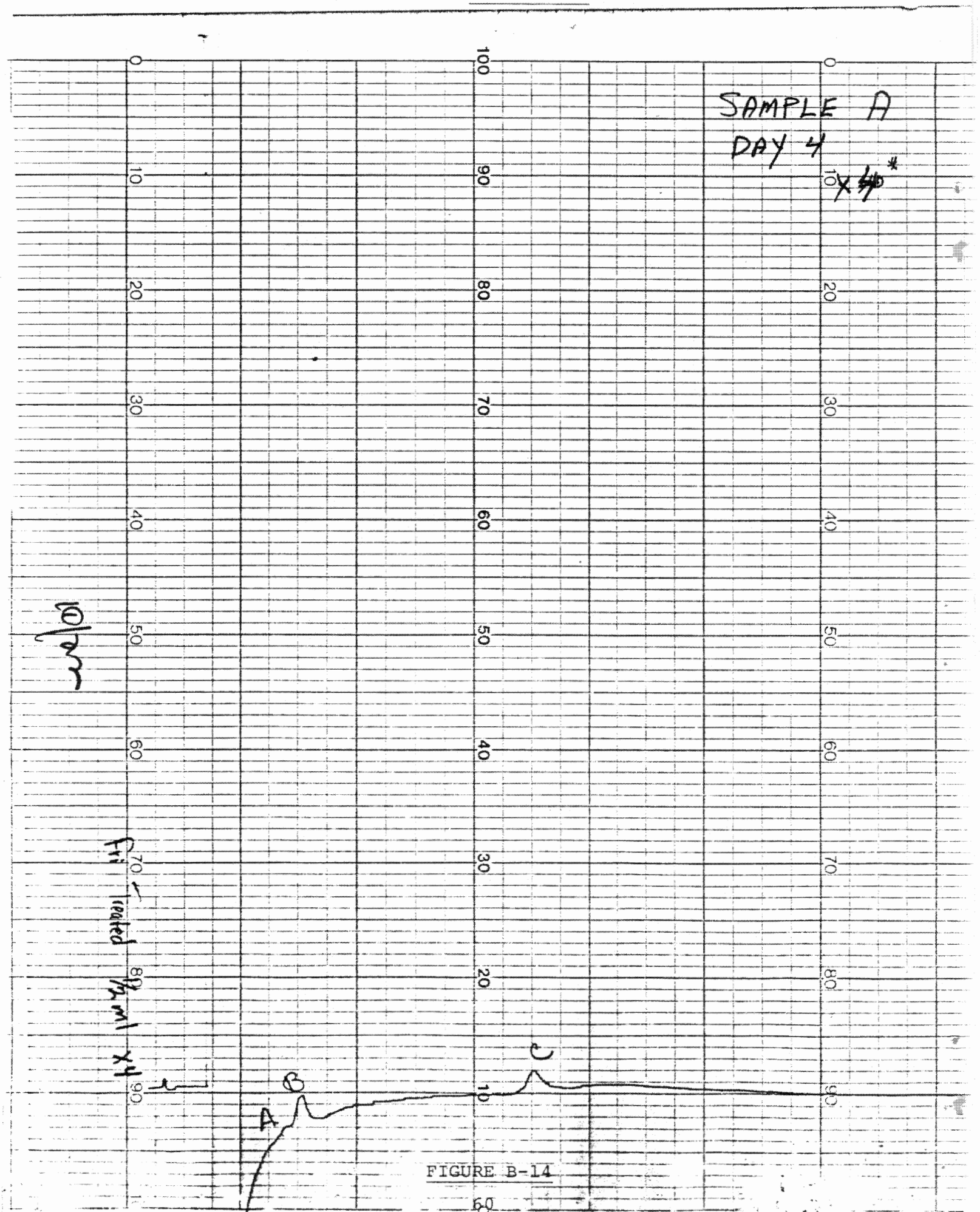


FIGURE B-14

*Sample A, DAY 4 at X40 not included as no diffrent than room air.

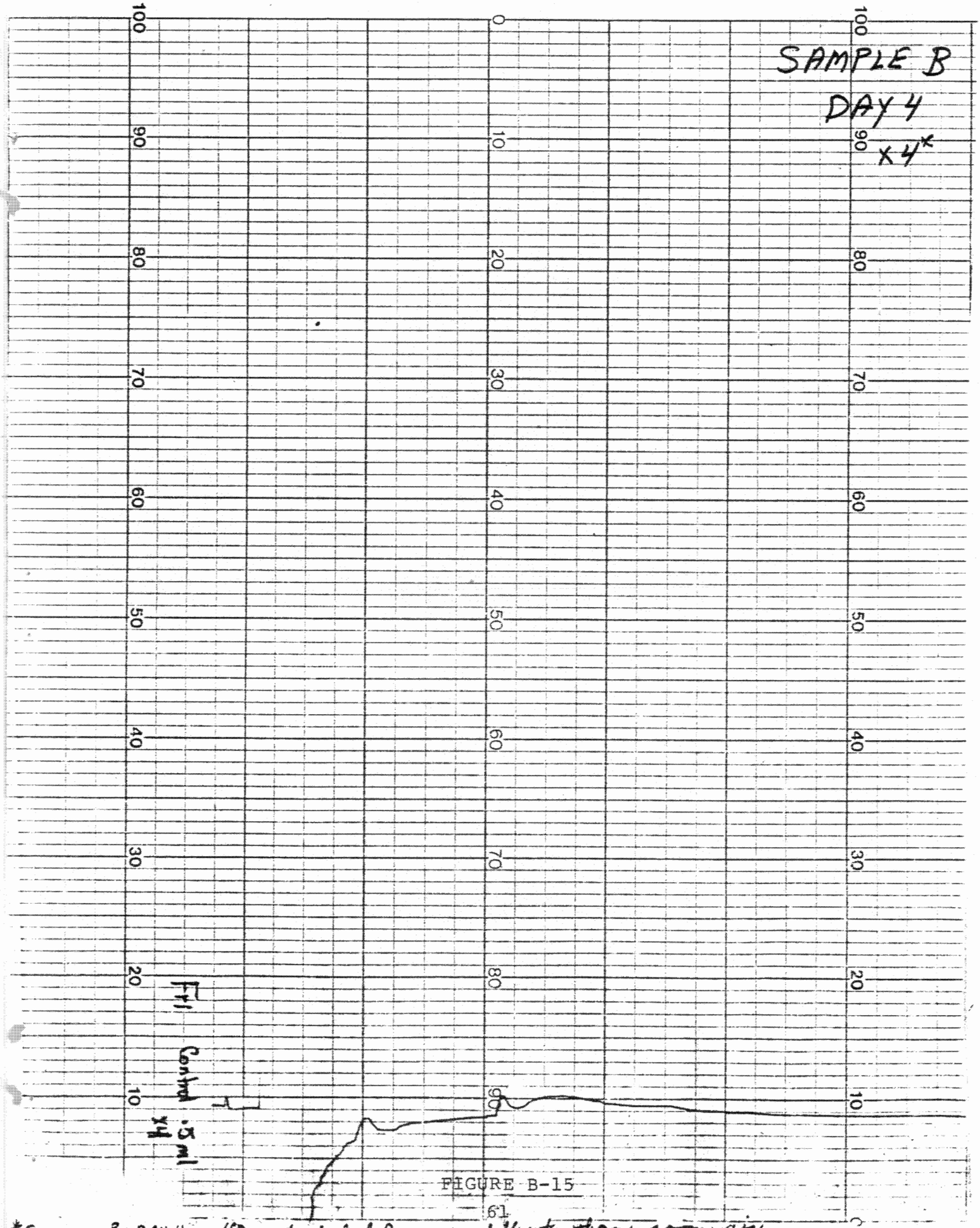


FIGURE B-15

*Sample B, DAY 4 x 40 not included. - no different than room air

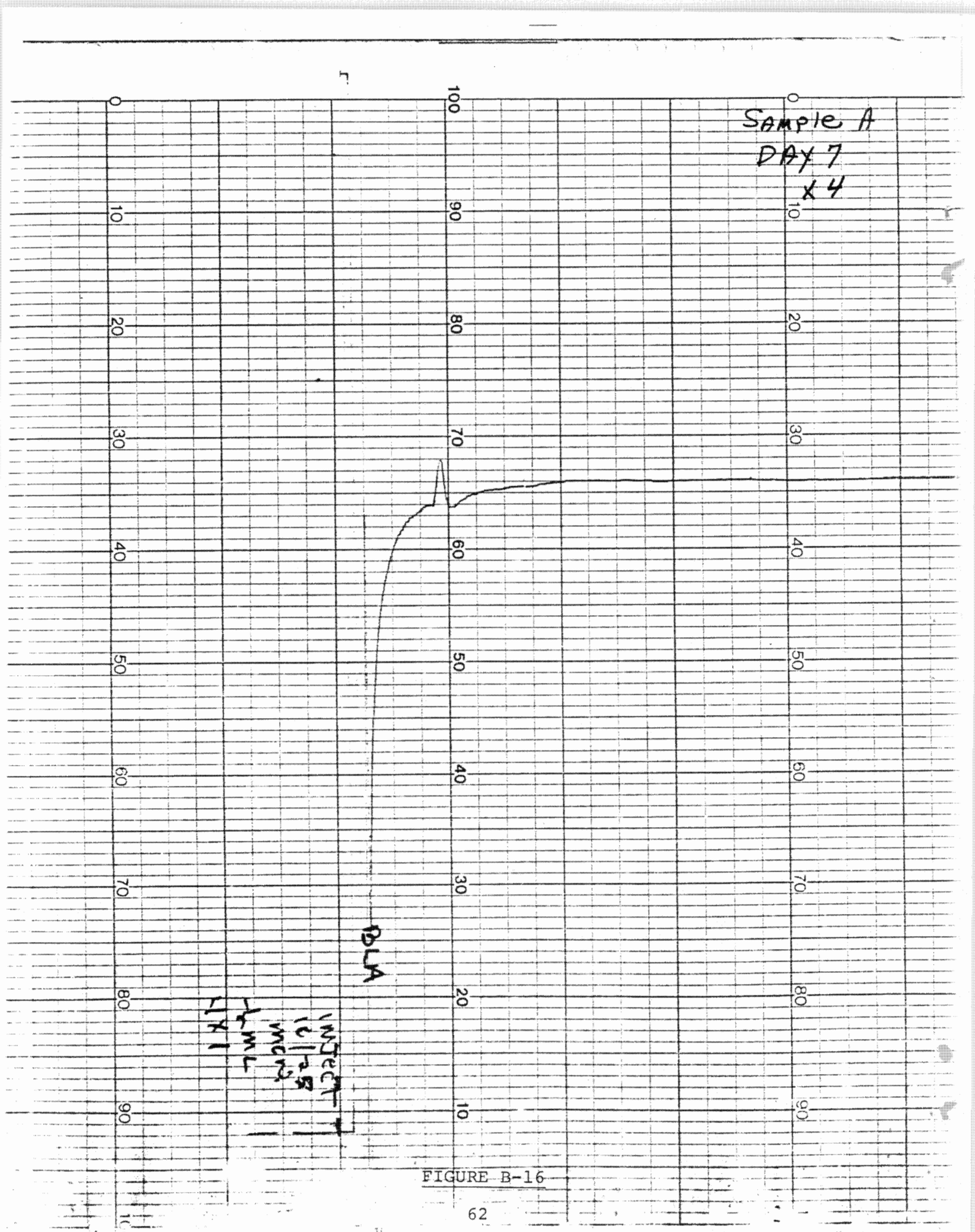


FIGURE B-16

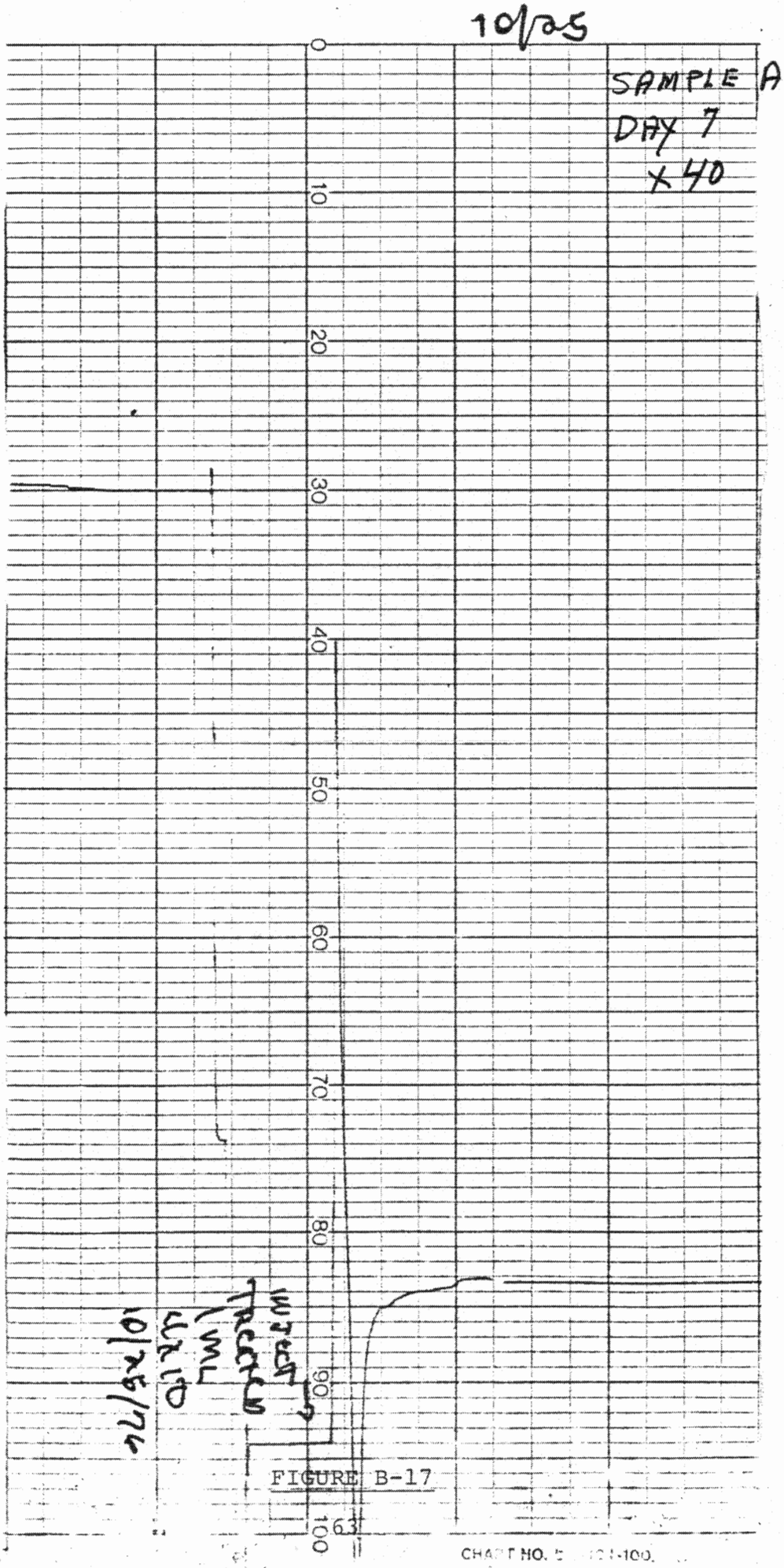


FIGURE B-17

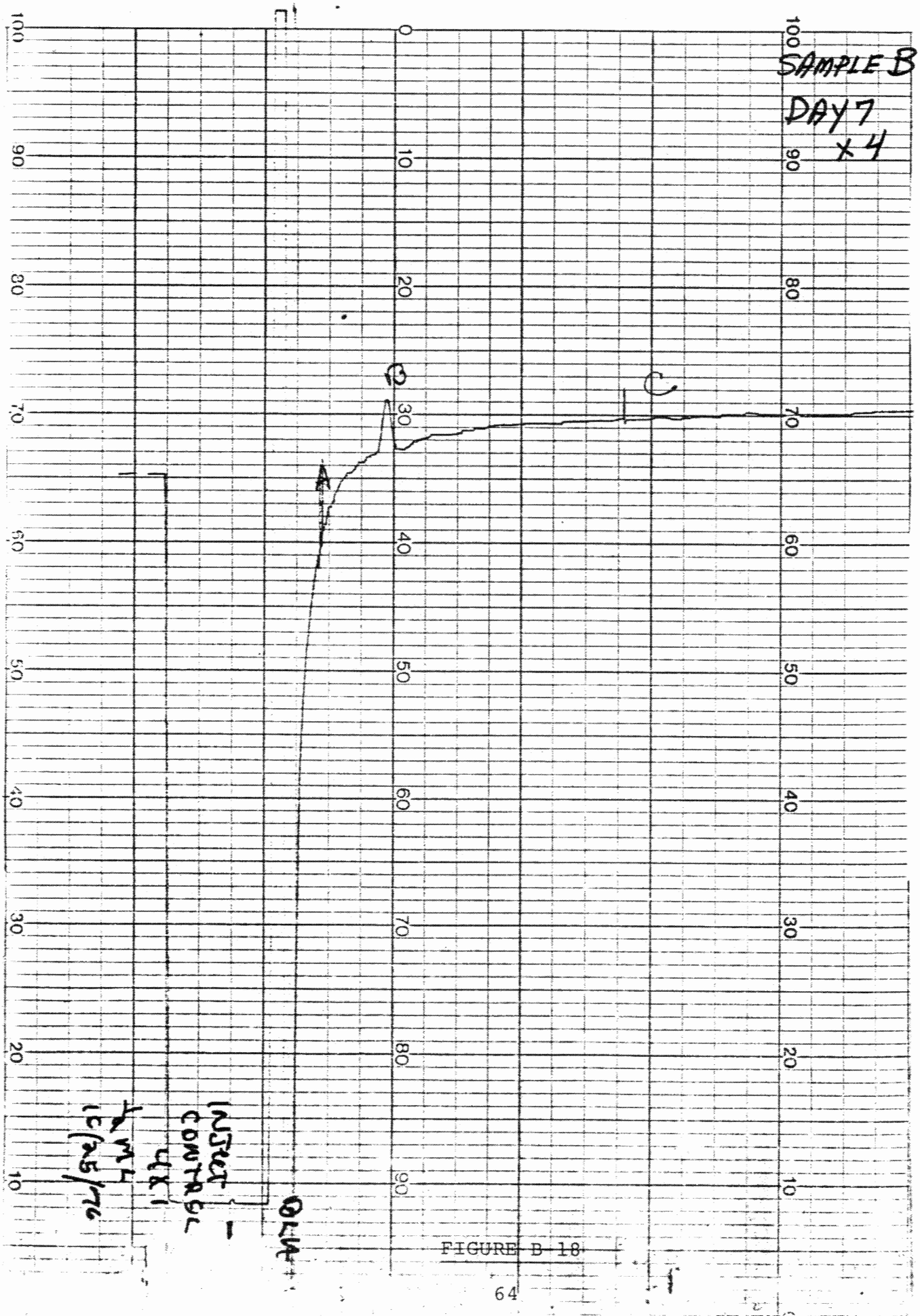


FIGURE B 18

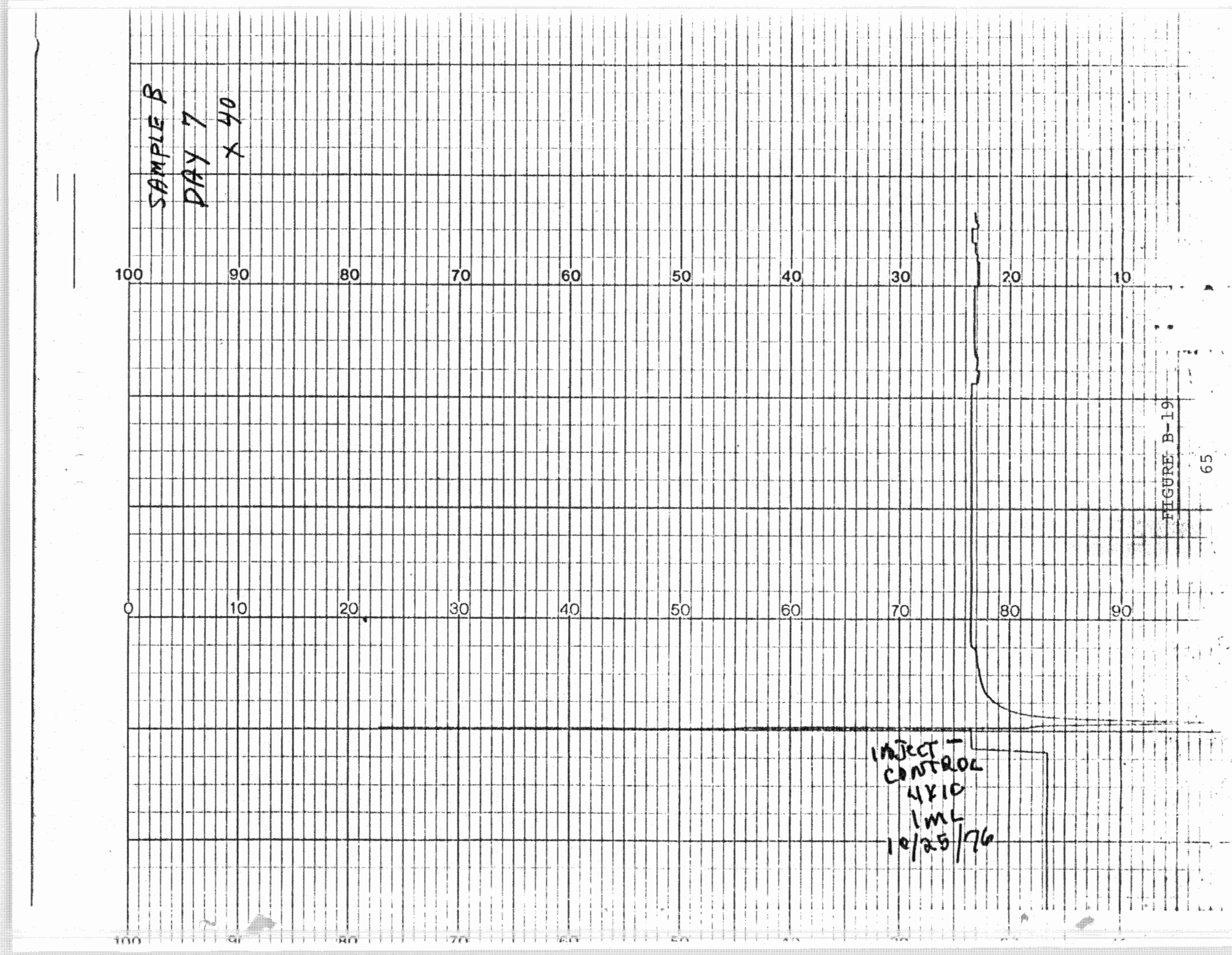

SAMPLE B
DAY 7
X 40
100
90
80
70
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
90
INJECT I
CONTROL
4X10
1ML
10/25/76

FIGURE B-19

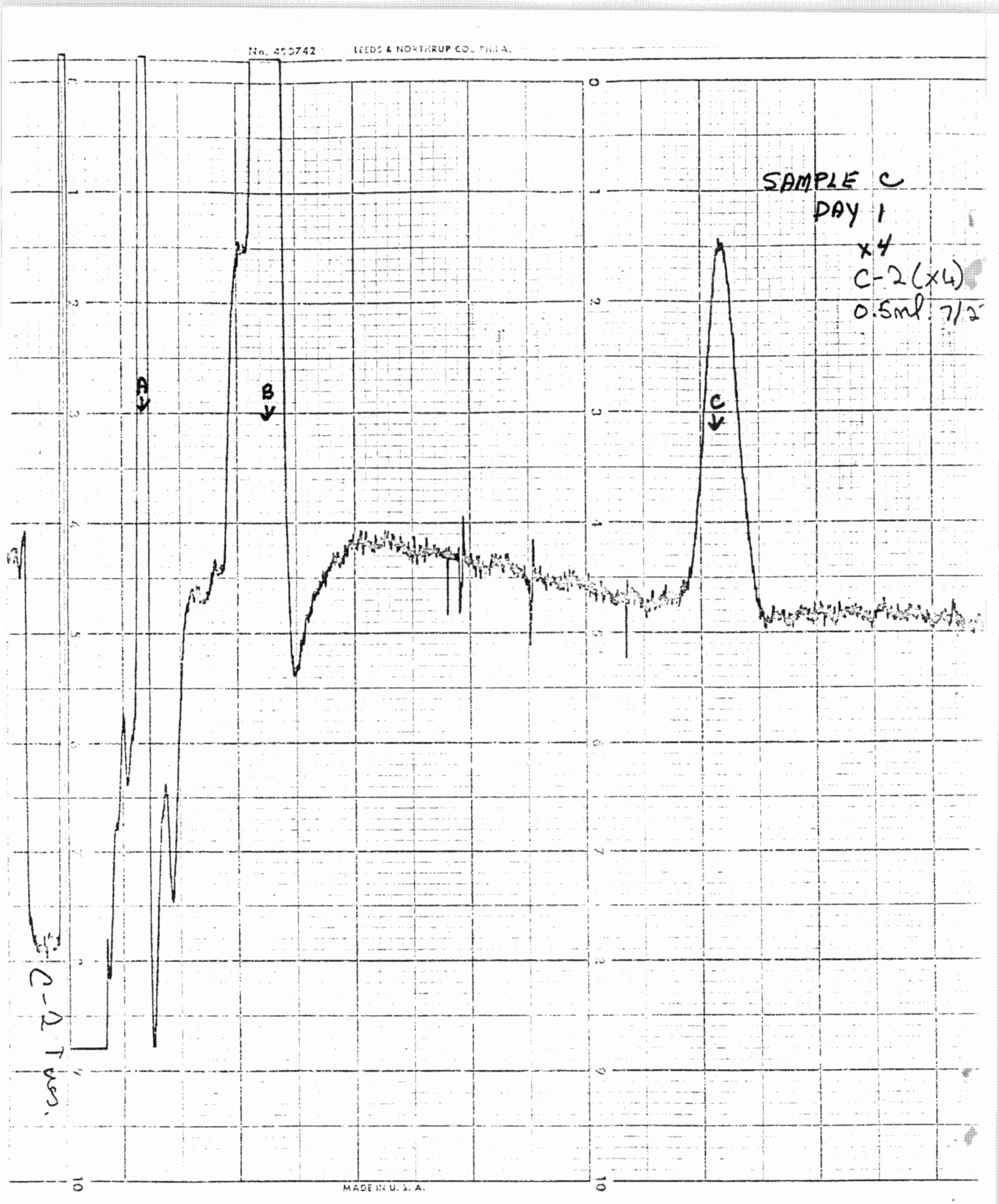

No. 450742 LEEDS & NORTHRUP CO., PHILA.
SAMPLE C
DAY 1
x4
C-2(x4)
0.5ml: 7/2
A
B
C
C-2 T aes.
MADE IN U. S. A.

FIGURE B-20

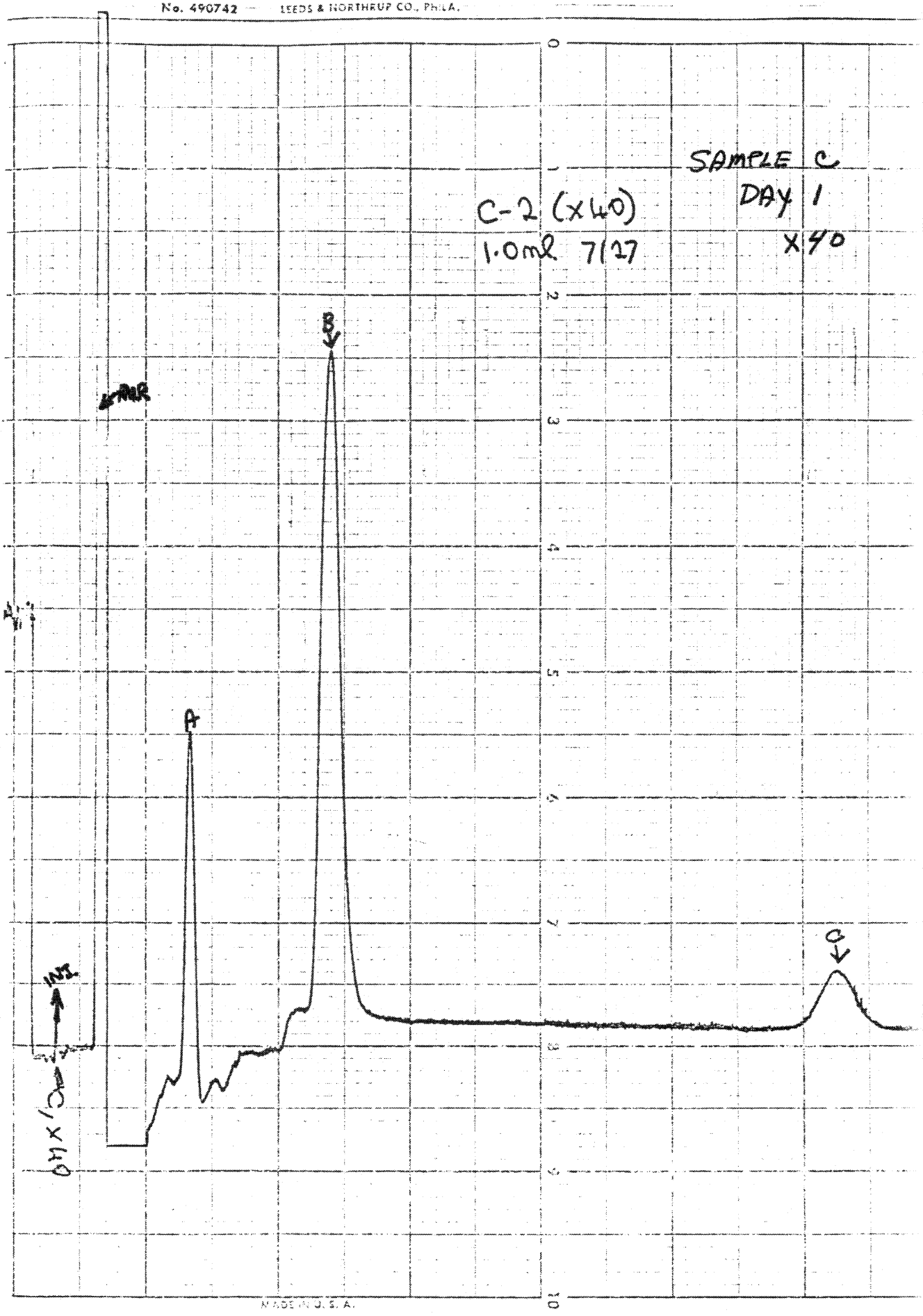

No. 490742 LEEDS & NORTHRUP CO., PHILA.
SAMPLE C
DAY 1
X40
C-2 (x40)
1.0ml 7/27
A
B
C
MADE IN U.S.A.

FIGURE B-21

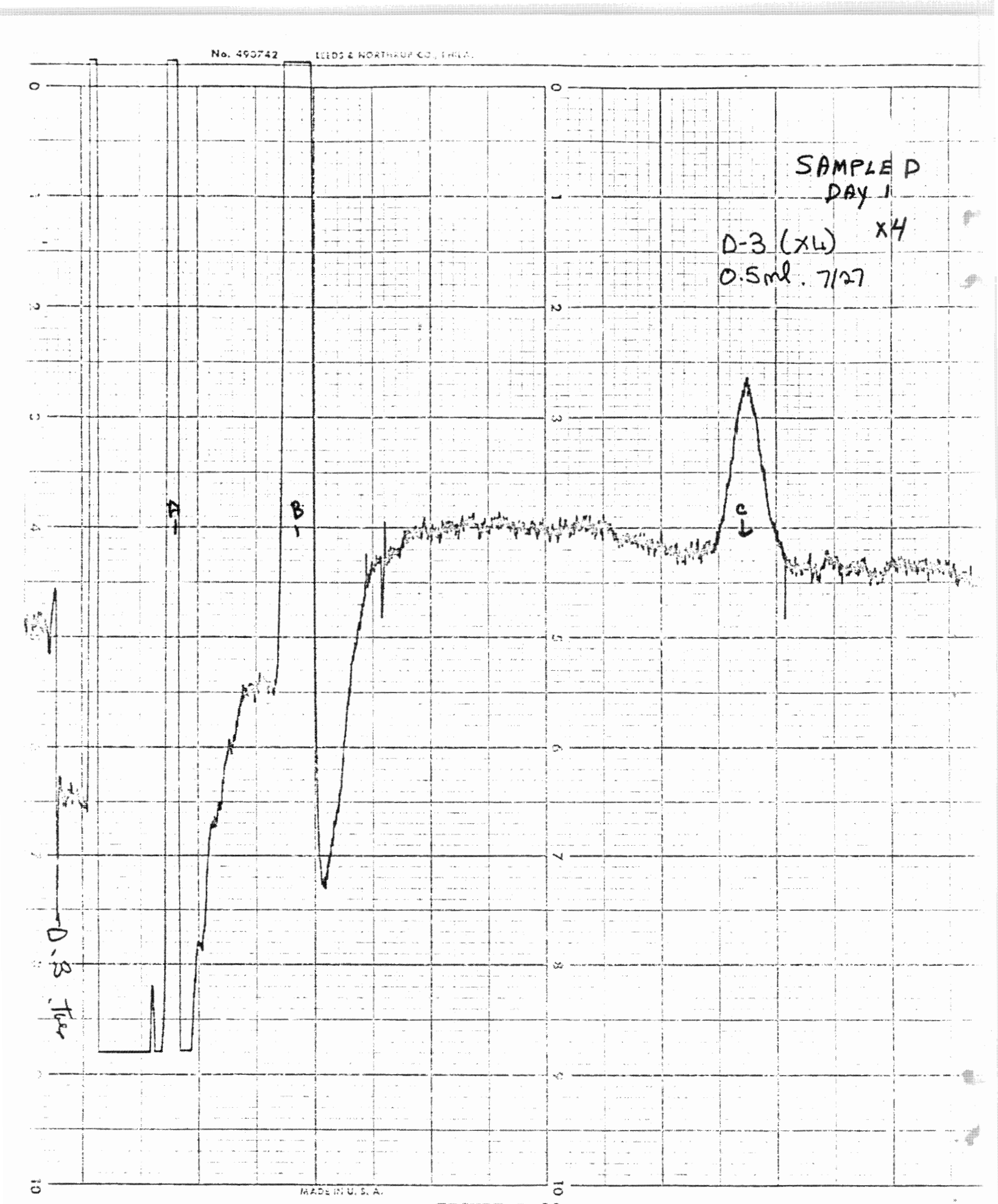

No. 490742 LEEDS & NORTHRUP CO., PHILA.
SAMPLE D
DAY 1
X4
D-3 (X4)
0.5ml. 7/27
A
B
C
D-B Tur
MADE IN U. S. A.

FIGURE B-22

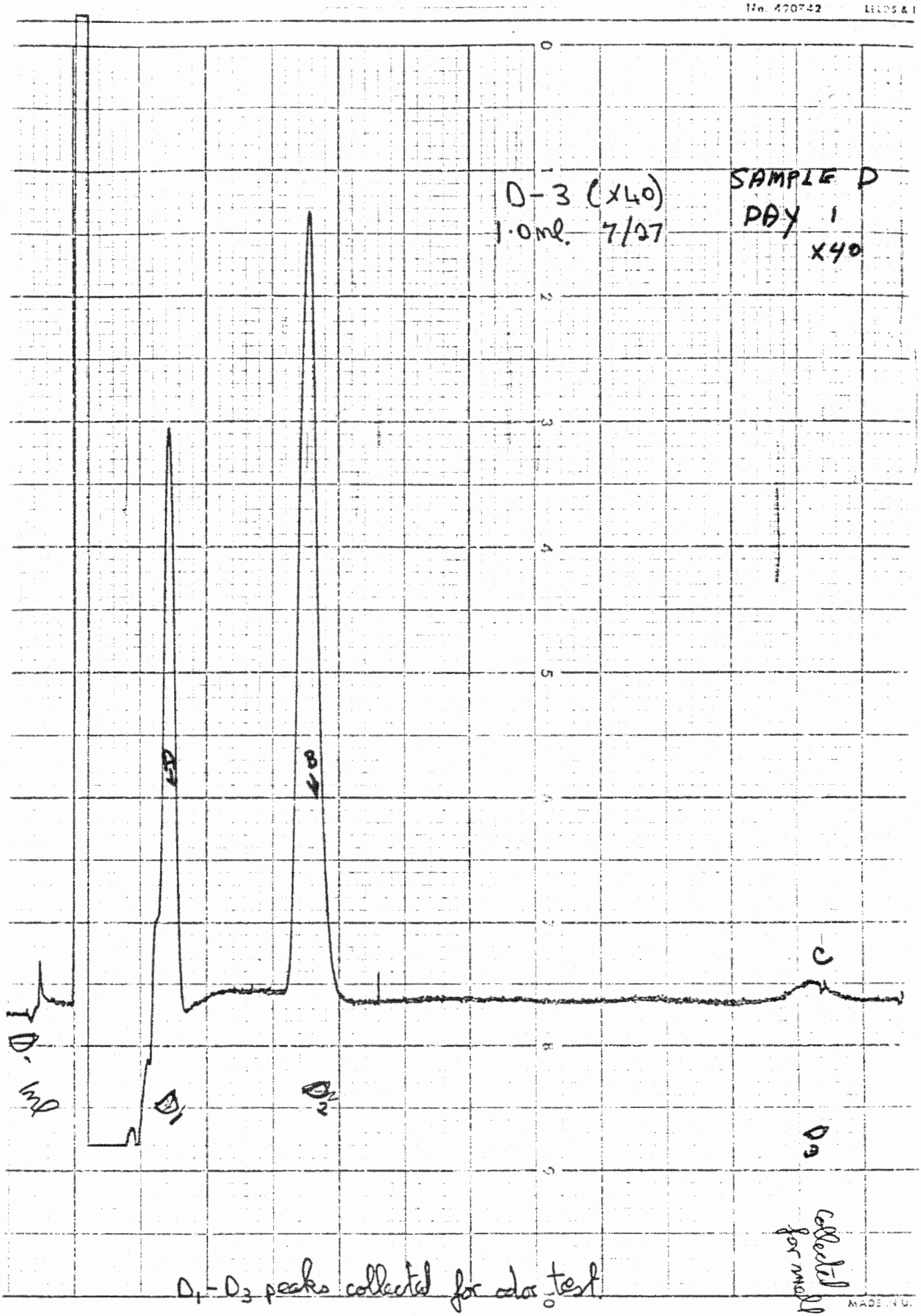

No. 420742 LEEDS & N
D-3 (X40)
1.0ml. 7/27
SAMPLE D
PBY 1
X40
A
B
C
D1
D2
D3
D1-D3 peaks collected for odor test.
collected for mobil.
MADE IN U.

FIGURE B-23

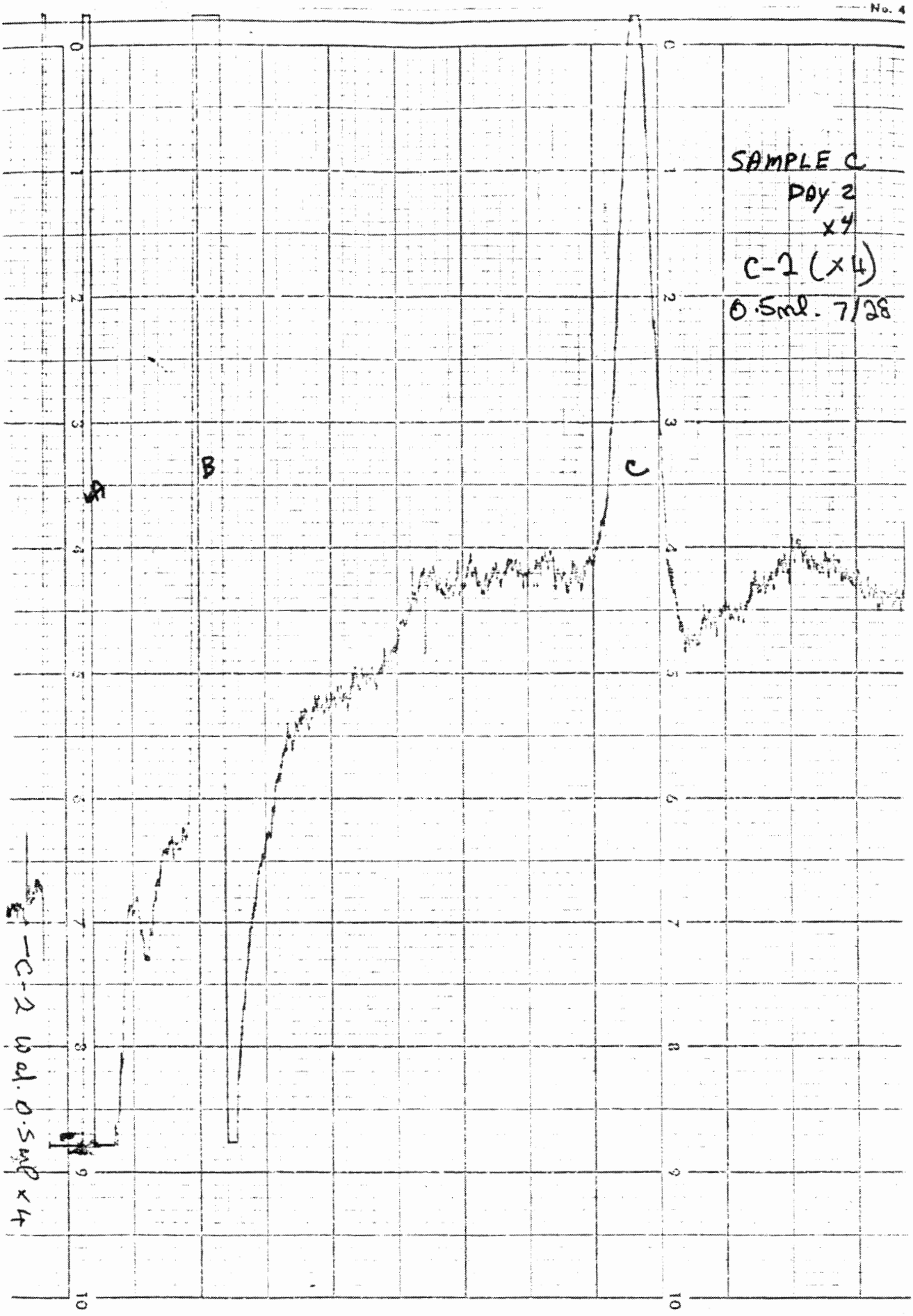


FIGURE B-24

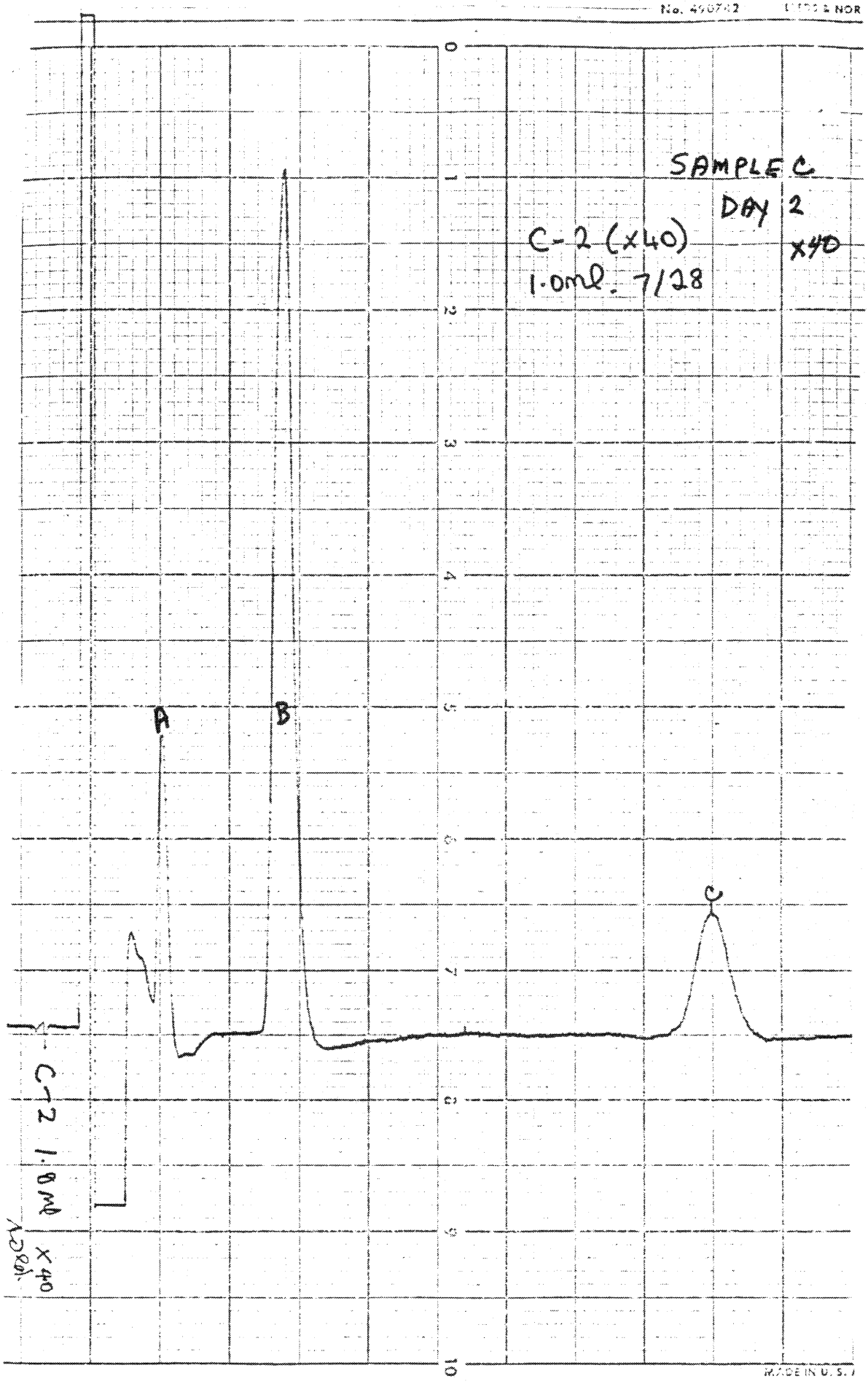


FIGURE B-25

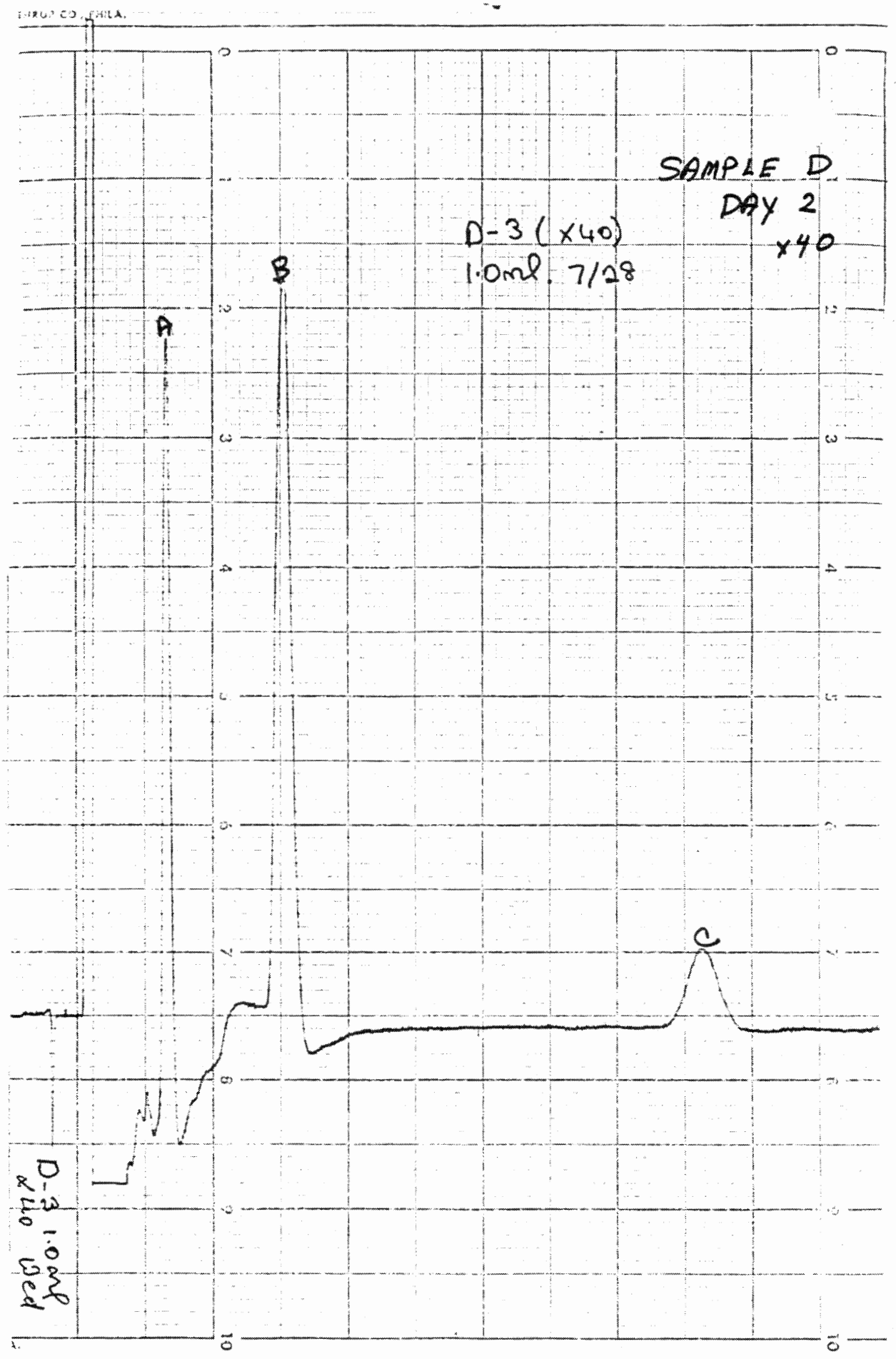


FIGURE B-26

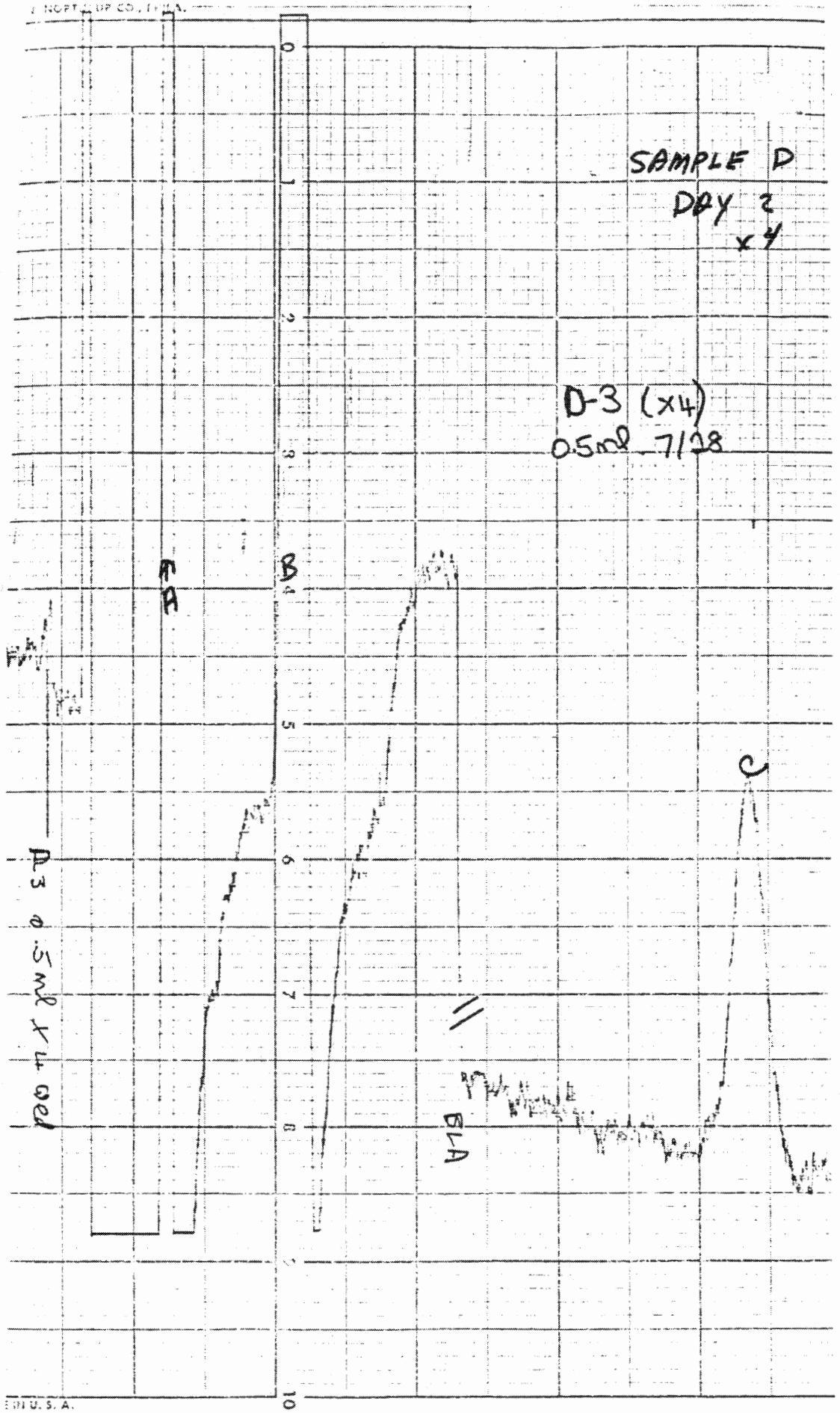


FIGURE B-27

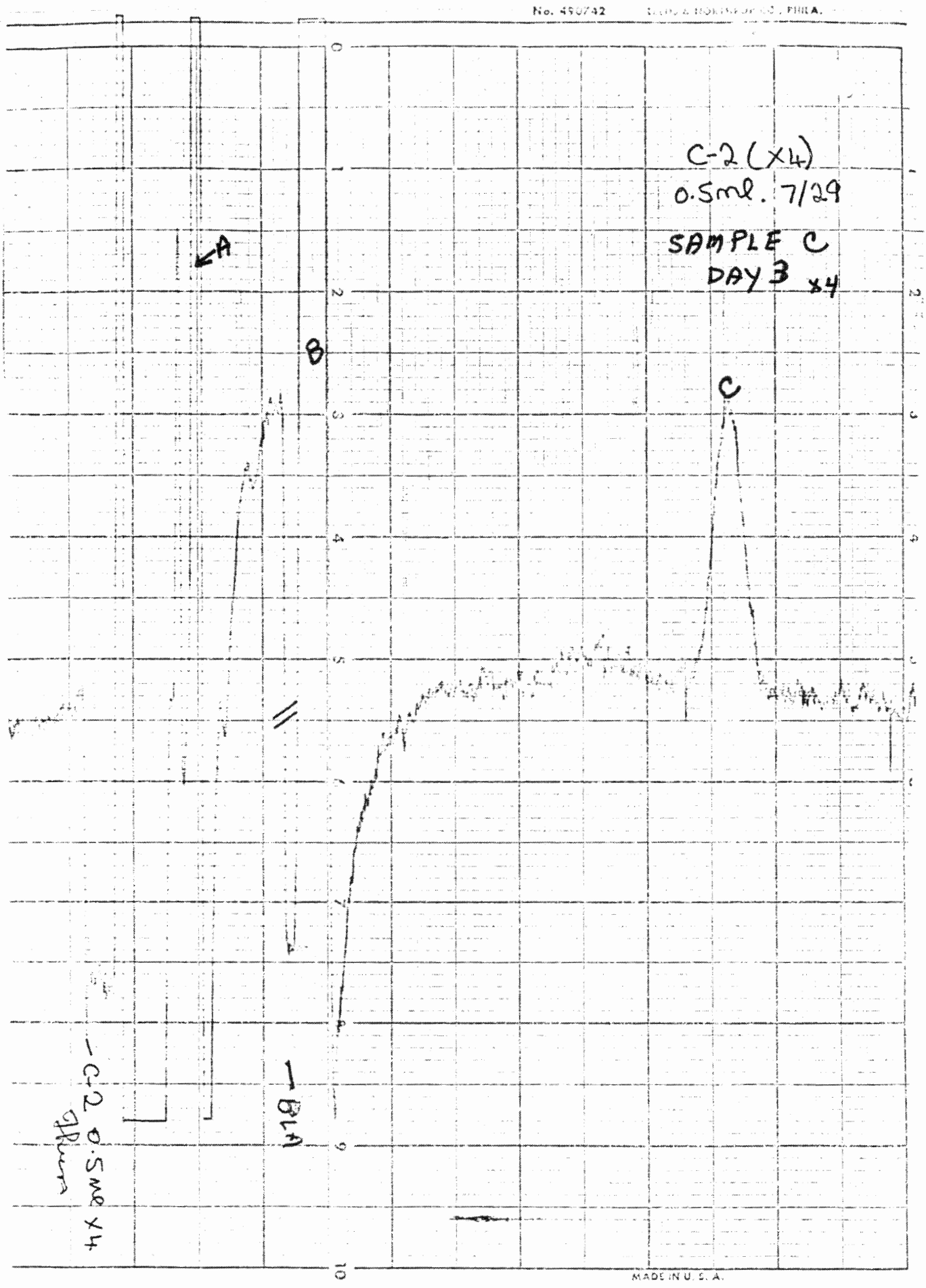

No. 450742
C-2 (X4)
0.5ml. 7/29
SAMPLE C
DAY 3 x4
A
B
C
BLA
C-2 0.5ml x4
MADE IN U. S. A.

FIGURE B-28

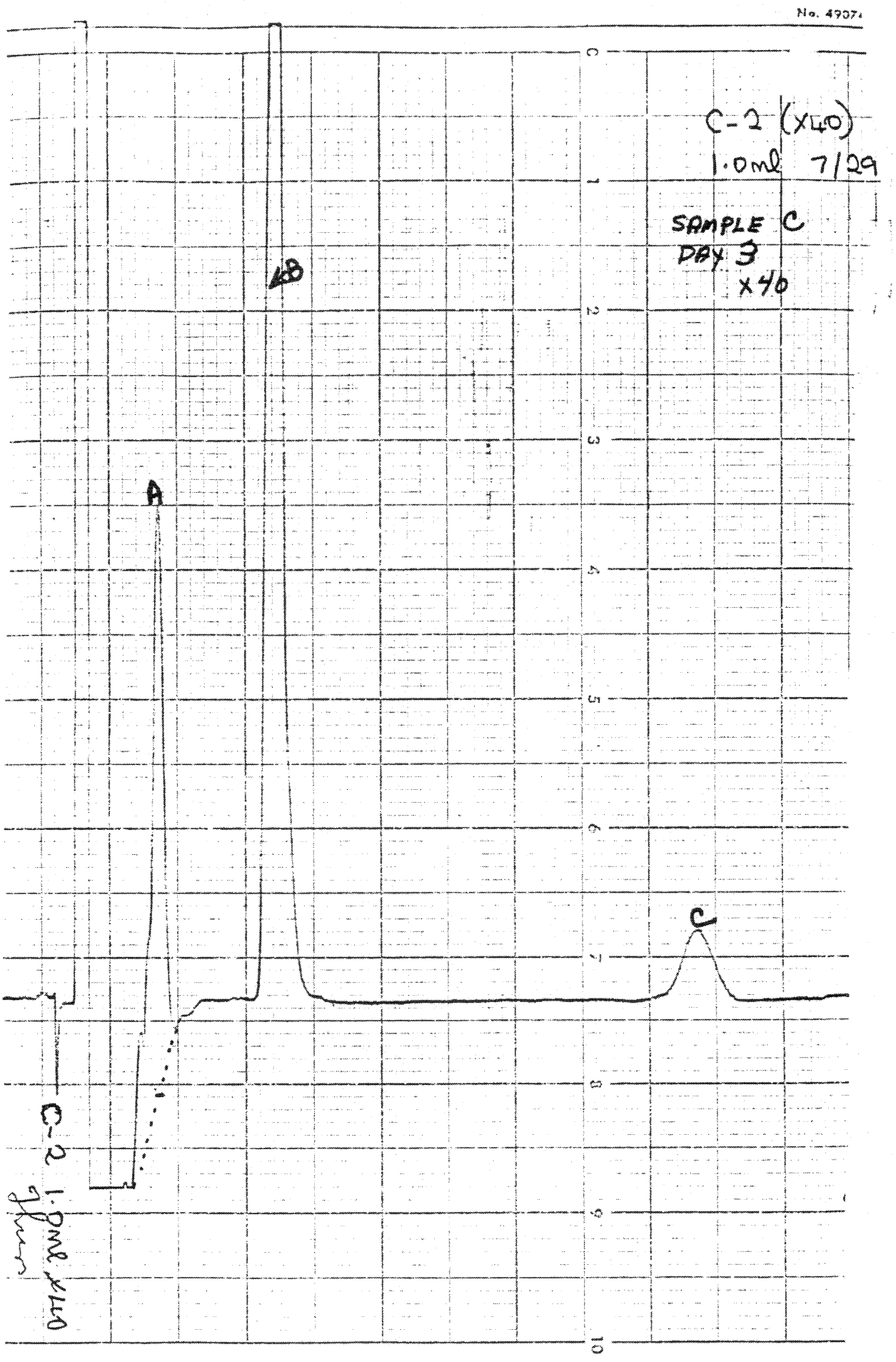

No. 4907
C-2 (x40)
1.0ml 7/29
SAMPLE C
DAY 3
x40
A
B
C
C-2 1.0ml x40
0
1
2
3
4
5
6
7
8
9
10

FIGURE B-29

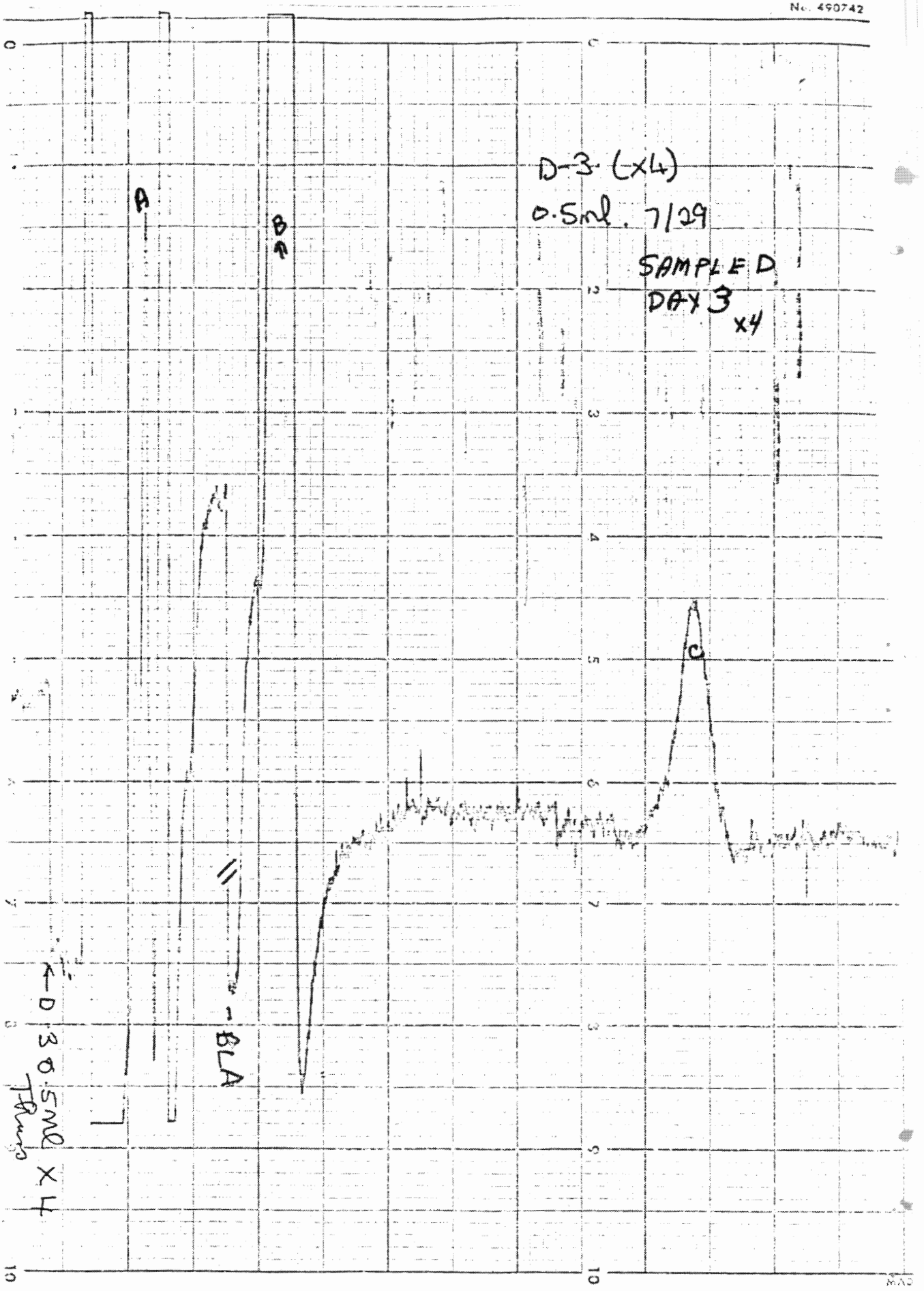

No. 490742
A
B
C
D-3 (x4)
0.5ml. 7/29
SAMPLED
DAY 3
x4
BLA
D 3 0.5ml
TRIS
X 4

FIGURE B-30

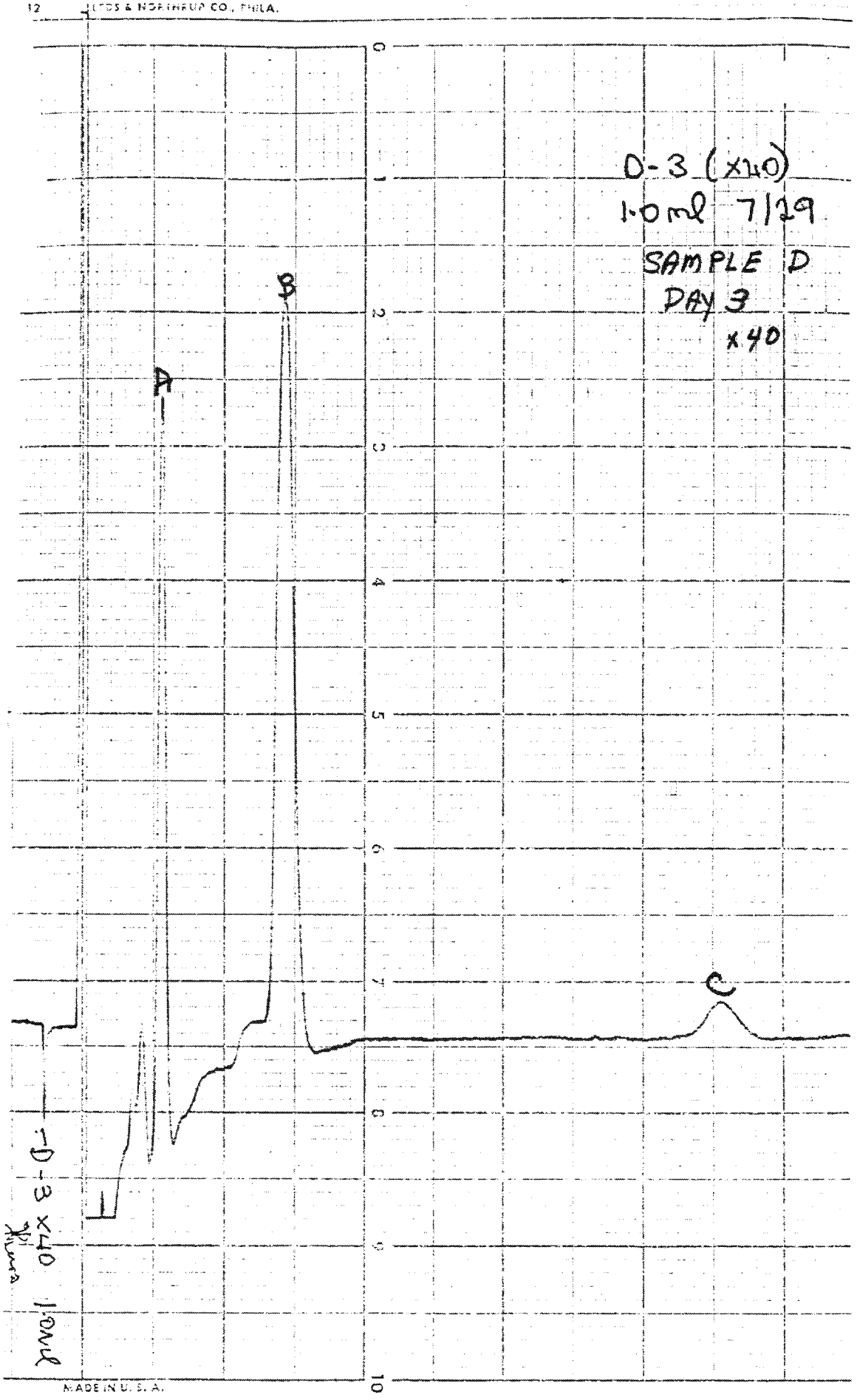

12 LEEDS & NORTHRUP CO., PHILA.
D-3 (x40)
1.0 ml 7/29
SAMPLE D
DAY 3
x40
A
B
C
D-3 x40 1/2 Alma 1/2 ml
MADE IN U. S. A.

FIGURE B-31

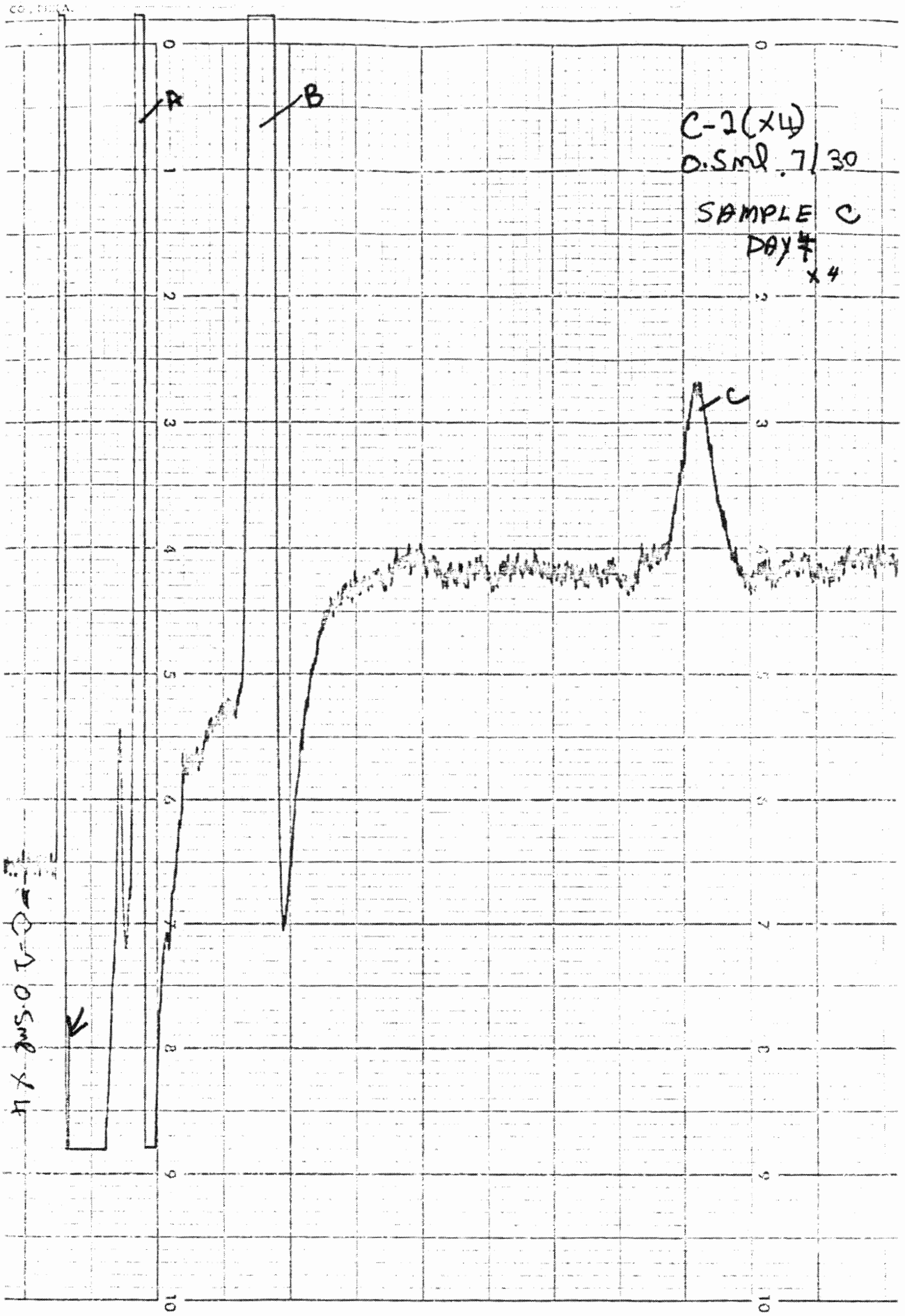


FIGURE B-32

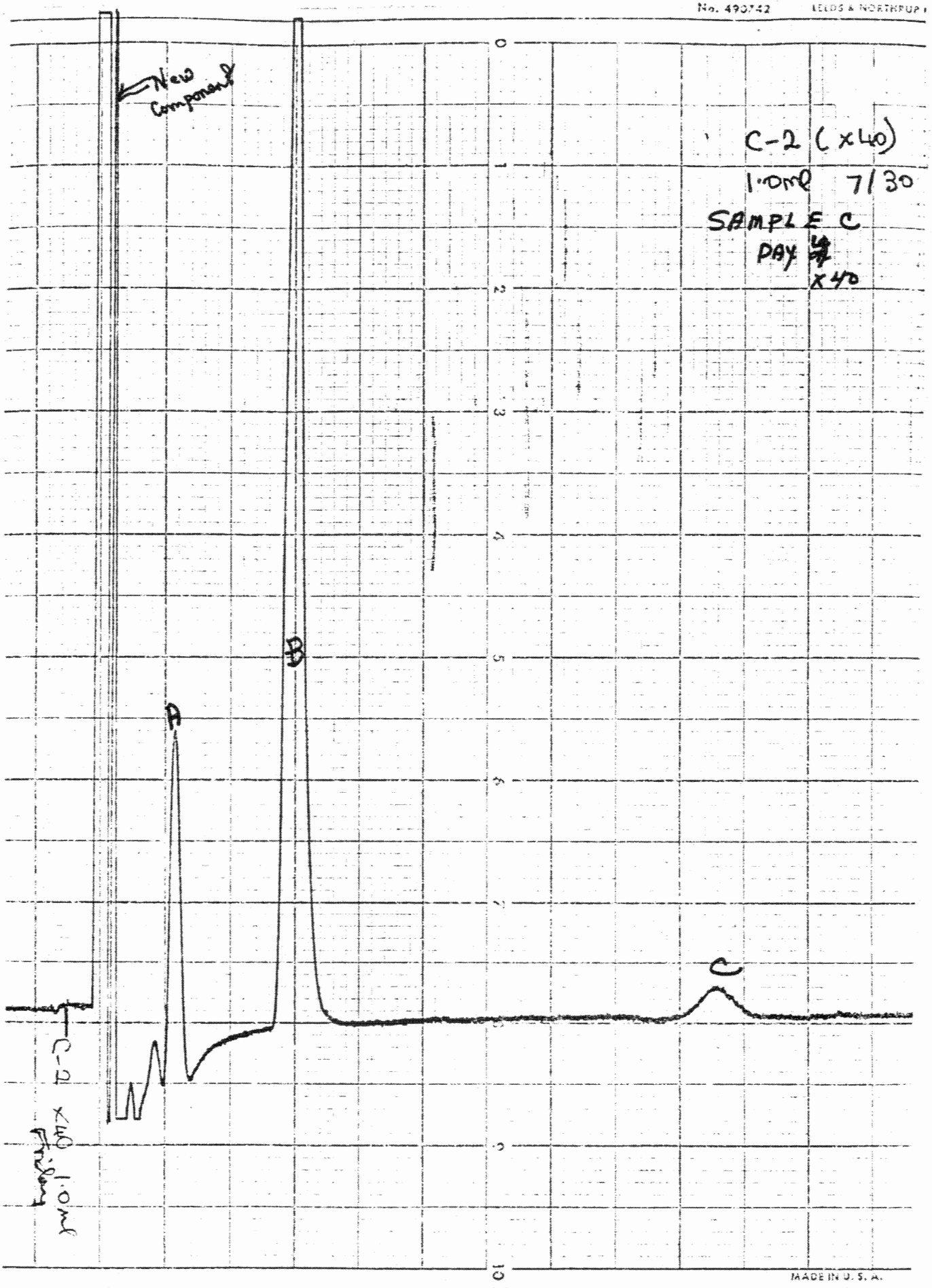

No. 490742
LEEDS & NORTHRUP
New Component
C-2 (x40)
1.0mℓ 7/30
SAMPLE C
DAY 4
x40
A
B
C
C-2 x40 1.0mℓ
MADE IN U. S. A.

FIGURE B-33

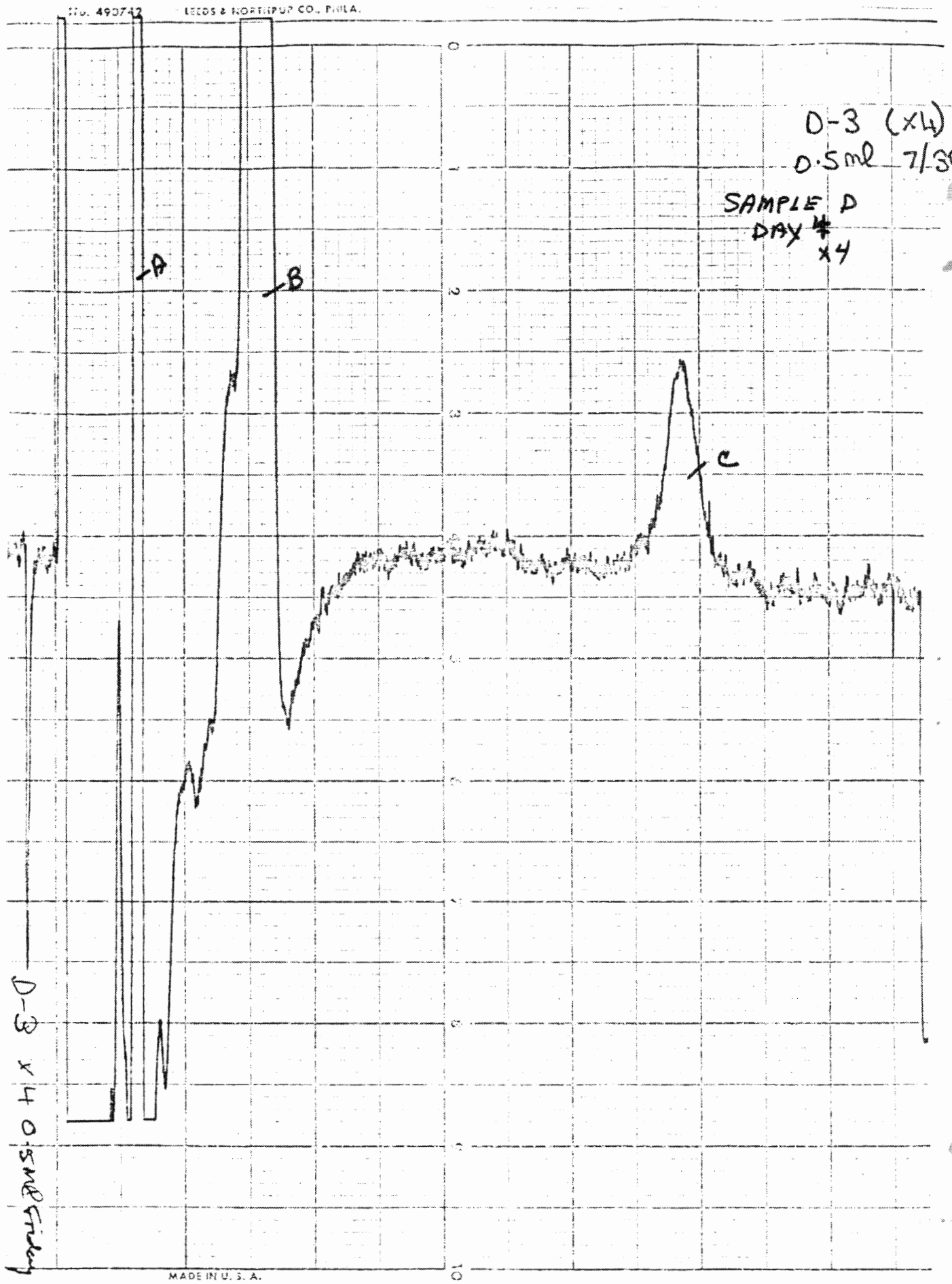

NO. 490742 LEEDS & NORTHRUP CO., PHILA.
D-3 (x4)
0.5ml 7/30
SAMPLE D
DAY 4
x4
A
B
C
D-3 x4 0.5ml Friday
MADE IN U. S. A.

FIGURE B-34

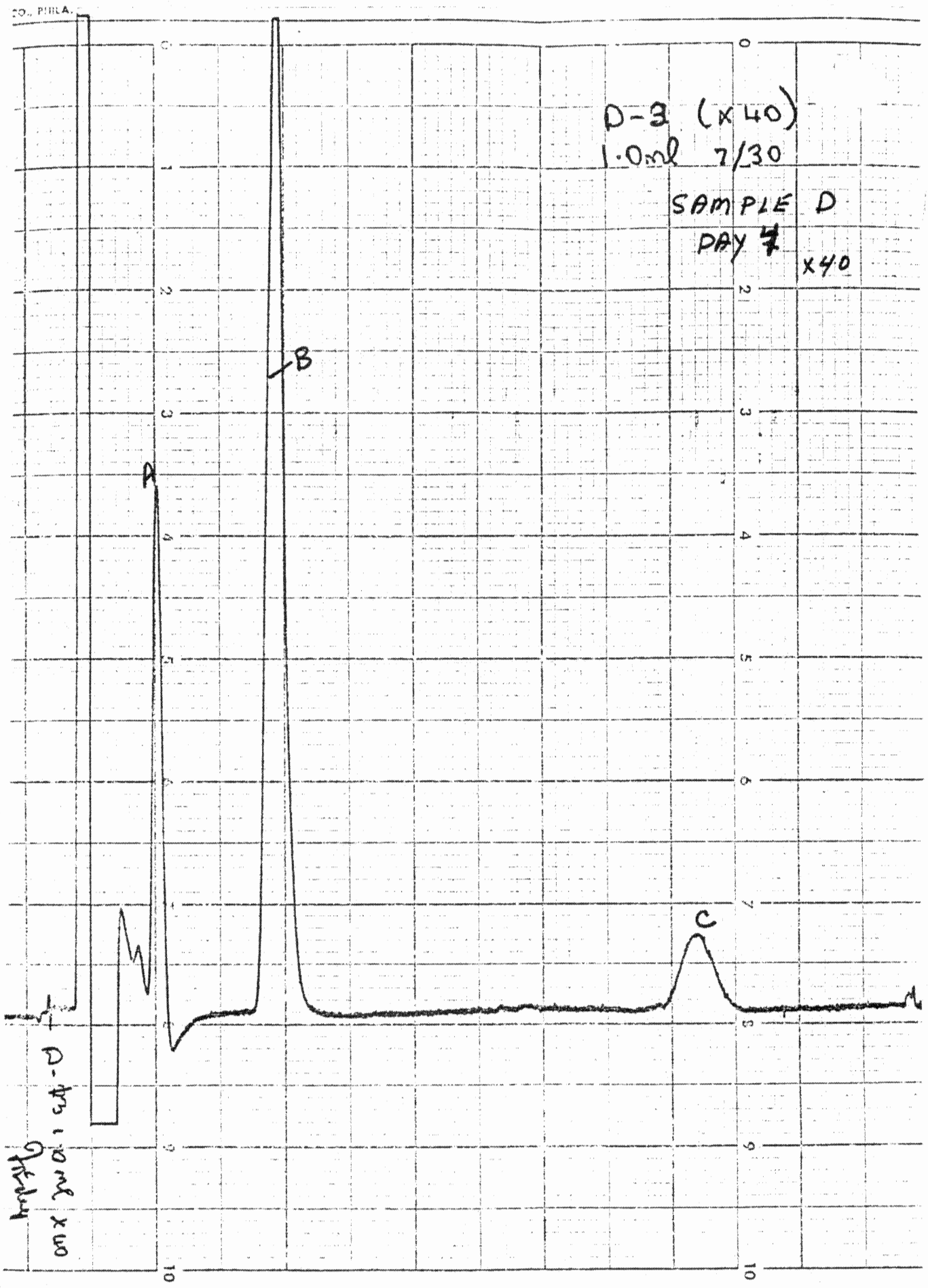


FIGURE B-35

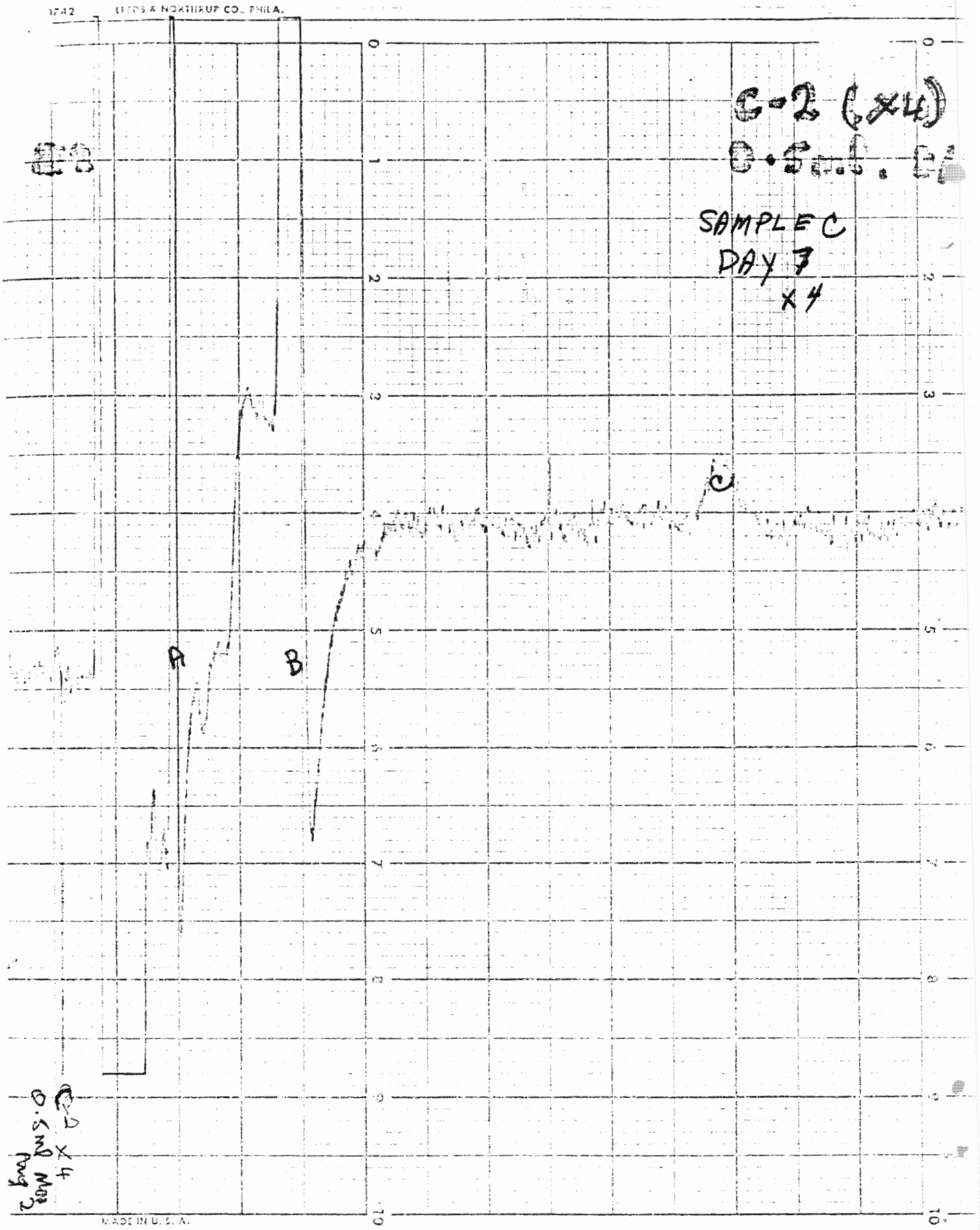

1742 LEEDS & NORTHRUP CO., PHILA.
C-2 (x4)
SAMPLE C
DAY 7
x4
A
B
C
MADE IN U. S. A.

FIGURE B-36

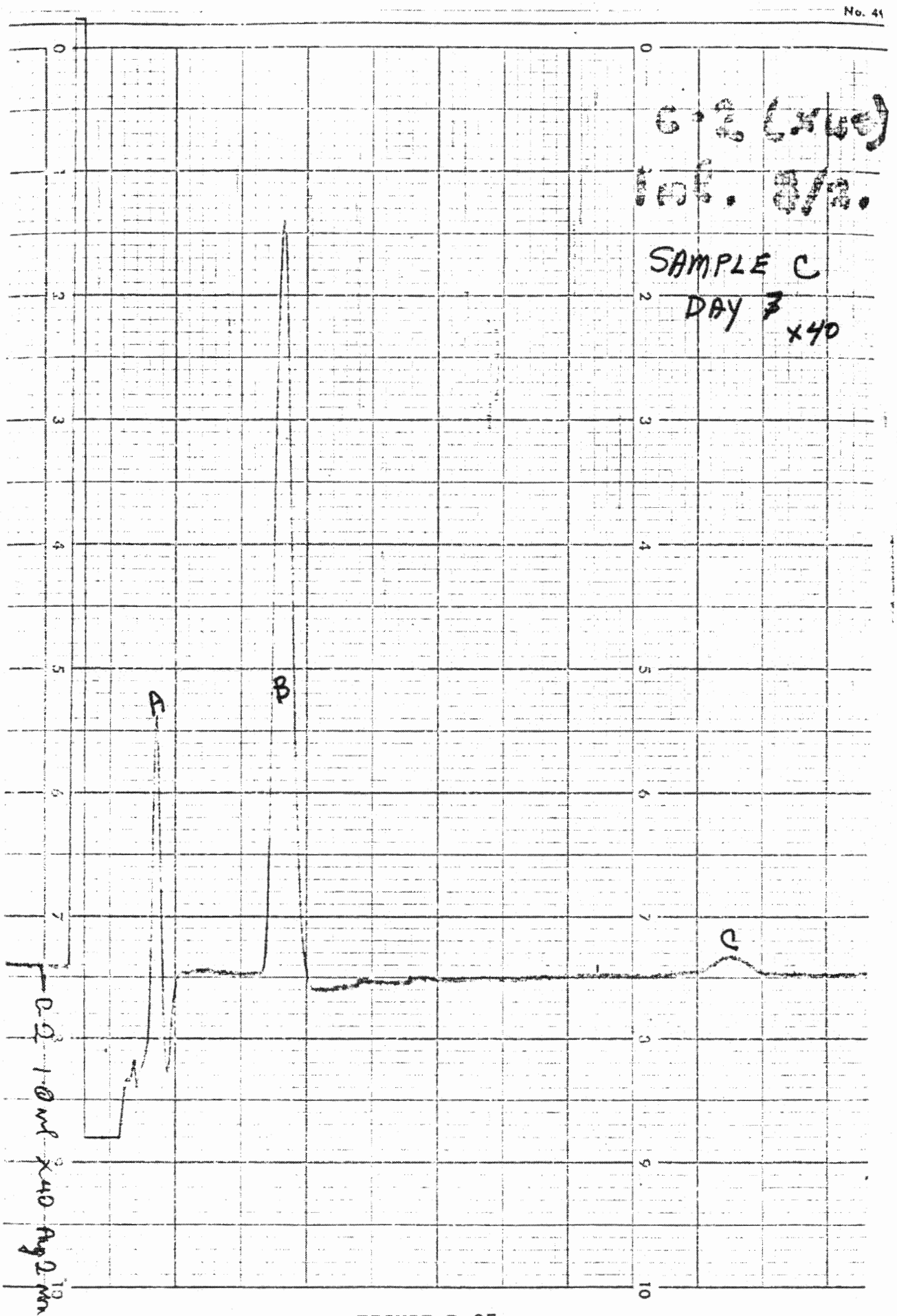


FIGURE B-37

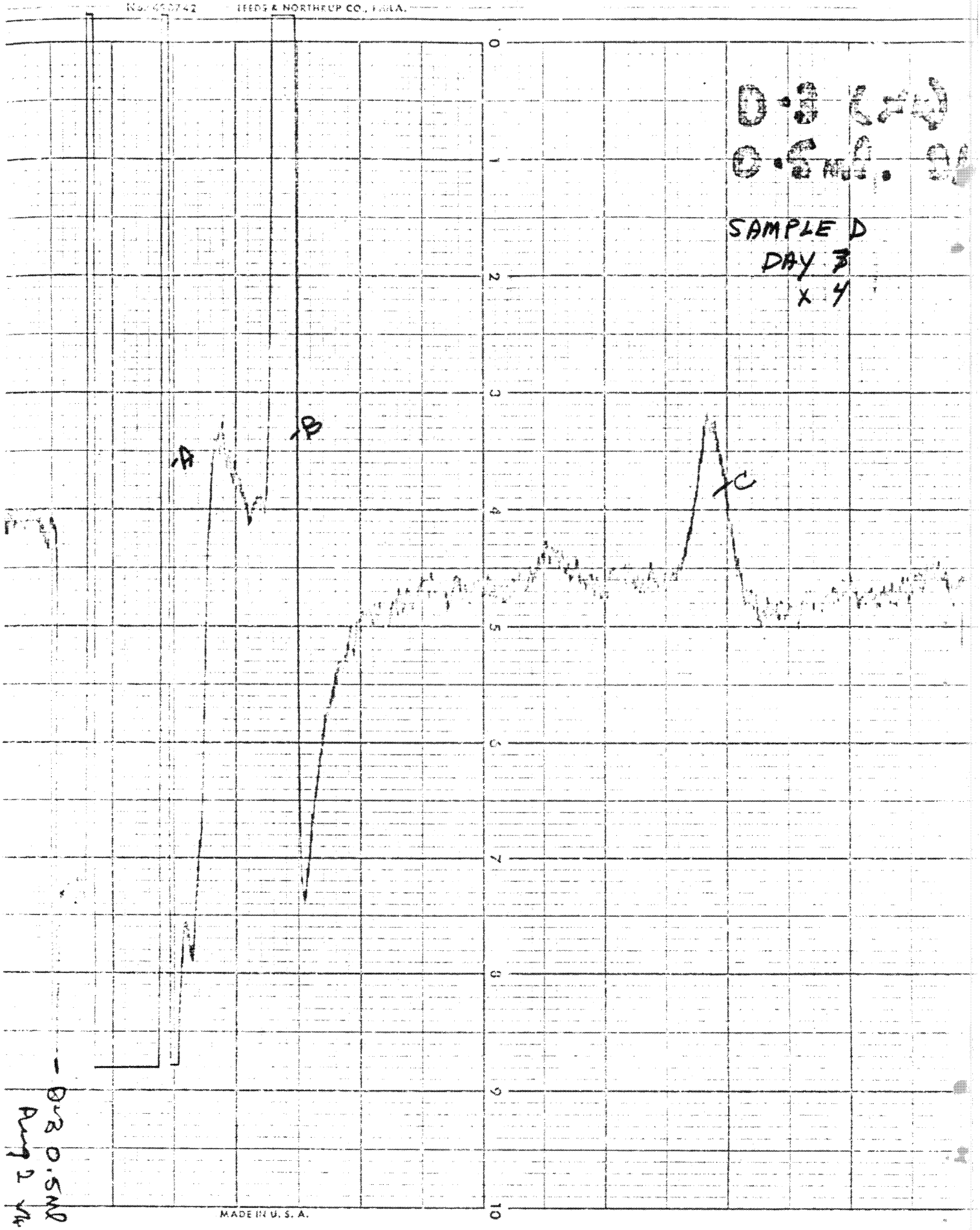

No. 660742 LEEDS & NORTHRUP CO., PHILA.
0
1
2
3
4
5
6
7
8
9
10
SAMPLE D
DAY 3
A
B
C
MADE IN U. S. A.

FIGURE B-38

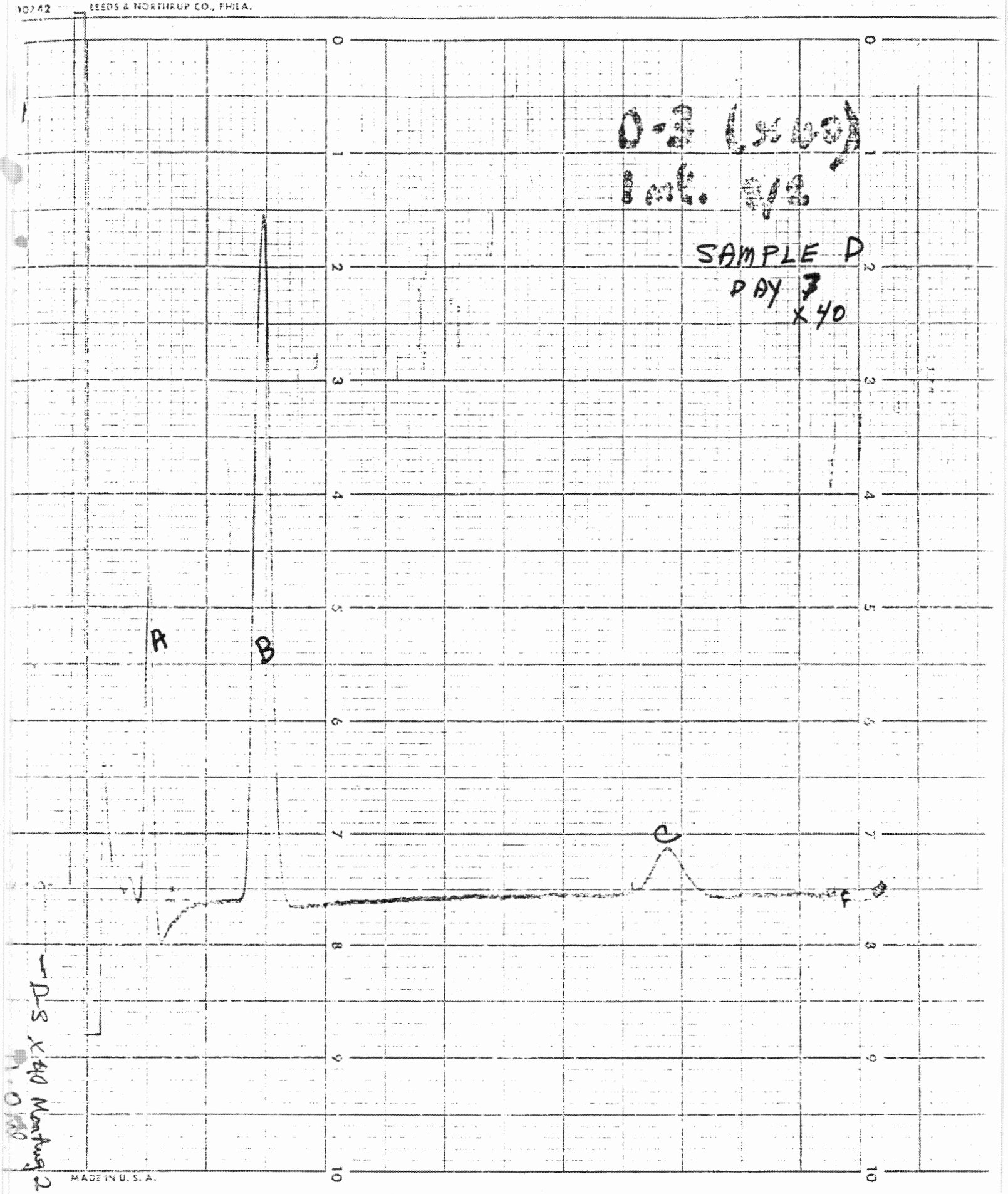


FIGURE B-39

BNWL-2177
UC-23
Odor Assessment
for Sewage Sludge
Samples

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