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## Photochemistry of Nitrous Acid and Nitrite Ion

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**PHOTOCHEMISTRY OF NITROUS ACID AND NITRITE ION**

**Kathryn E. Shanks**

**Advisor: Timothy R. Rettich**

**Chemistry 499 Thesis**

**Illinois Wesleyan University**

**May 6, 1993**



Approval Page

"Photochemistry of Nitrous Acid and Nitrite Ion"

by Kathryn E. Shanks

A paper submitted in partial fulfillment of the requirements  
for Chemistry 499 and Honors in Chemistry

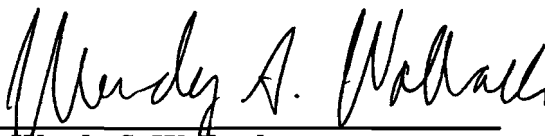
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Dr. David N. Bailey



Dr. Wendy S. Wolbach



Sister Helen Carey

Illinois Wesleyan University

1993

"I do not know what I may appear to the world; but to myself I seem to have been only like a boy playing on the sea-shore, and diverting myself in now and then finding a smoother pebble or prettier shell than ordinary, whilst the great ocean of truth lay all undiscovered before me."

-Sir Isaac Newton

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## ABSTRACT

Research is currently underway to elucidate the photochemical decomposition mechanism of nitrous acid and nitrite ion in aqueous and non-aqueous media. The quantum yield of the photochemical disappearance of nitrous acid and nitrite, as a function of pH and nitrous acid/nitrite ion concentration ratios, was examined. Spectroscopic studies have been done with nitrite ion in various aprotic organic solvents. Similar work has been started with molecular nitrous acid that was produced in aqueous solution and then extracted into organic solvents. These organic solvents were employed in order to study the quantum yield with respect to  $\text{NO}_2^-$  and HONO without the complications of the acid dissociation equilibrium seen in aqueous solutions. Other work includes the product analysis of hydroxyl radical scavenging reactions.

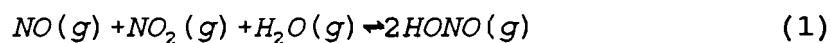
## INTRODUCTION AND THEORY

The purpose of this research is to investigate the photochemistry of the nitrous acid (HONO)/nitrite ion ( $\text{NO}_2^-$ ) system in both aqueous and non-aqueous (non-equilibrium) media. The quantum yield of the photochemical disappearance of each species (HONO and  $\text{NO}_2^-$ ) is desired. In addition, quantitative analysis of the reaction products by spectroscopic, chromatographic, and other analytical techniques is undertaken.

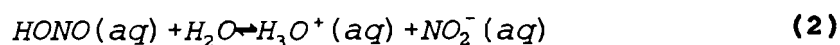
This research is significant because it adds to the limited chemical knowledge about nitrous acid. Nitrous acid is of interest because it is a known producer of atmospheric hydroxyl radical.<sup>1</sup> Hydroxyl radical, in turn, with hydrogen peroxide and ozone is involved in the photochemical oxidation of sulfur dioxide and hydrocarbons in the atmosphere.<sup>2,3</sup> The oxides of nitrogen, including nitrous acid and nitrite ion, are also well known catalysts in the production of sulfuric acid, the major component of acid rain. So, any additional understanding of nitrous acid chemistry could in fact be the key to solving several interrelated environmental problems including depletion of the ozone layer, formation of smog, and production of acid rain.

Nitrous acid appears to undergo several different types of reactions including thermal reactions and photochemical reactions. Of the thermal reactions, some were studied in the gaseous phase while others were done in the liquid phase. The gas phase reactions of nitrous acid were first studied by Cox and Atkins in 1973.<sup>4</sup> They proposed that nitrous acid is in equilibrium with nitric

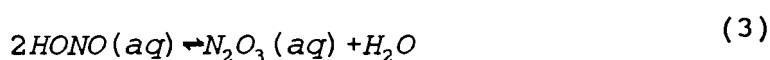
oxide and nitrogen dioxide as shown in equation 1:



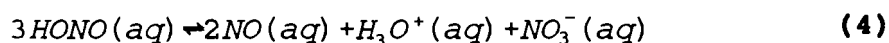
In aqueous medium, there are two recognized equilibria, the acid dissociation reaction shown in equation 2:



and the dehydration reaction shown in equation 3:



Another decomposition reaction was actively studied by Ray *et al.*<sup>5</sup> and is shown in equation 4:



The dehydration and acid dissociation reactions rapidly achieve equilibrium, but the decomposition by reaction 4 has a half life of about 14 hours at 0°C.

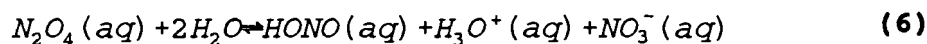
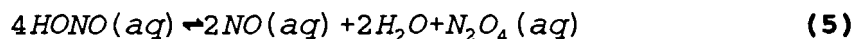
Therefore, the rate of decomposition is significant and must be accounted for in any photochemical studies.

The first kinetic studies of reaction 4 were performed by Montemartini in 1890.<sup>6</sup> He found the stoichiometry and kinetic order with respect to nitrous acid. He determined that the reaction showed first order kinetics at low nitrous acid concentrations and 2.5 order at high nitrous acid levels. The low concentration work has been reproducible.<sup>5,7,8</sup> The high concentration results, however, have not been confirmed. Reported values for the kinetic order have varied from 2.5 up to

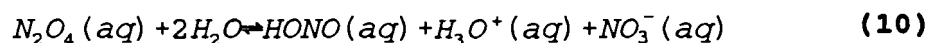
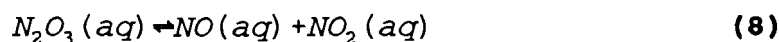
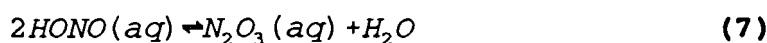


4.<sup>7,8,9</sup>

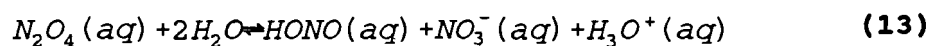
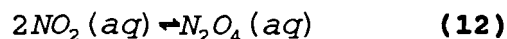
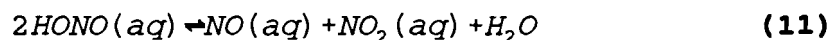
Two possible decomposition mechanisms for the higher nitrous acid concentrations were proposed by Abel and Schmid in 1928.<sup>9</sup> They are:



and



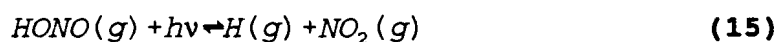
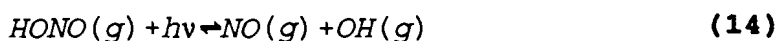
Thie proposed another possible mechanism in 1947:<sup>10</sup>



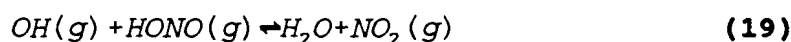
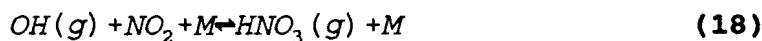
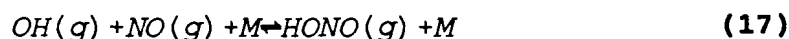
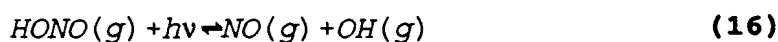
All three of these decomposition mechanisms share the same final step, the hydrolysis of dinitrogen tetroxide. The later studies of Usubillaga<sup>7</sup>, Rettich<sup>8</sup>, and Park *et al.*<sup>11</sup> fail to distinguish between these mechanisms.

Nitrous acid can also undergo reactions by photochemical means. Again,

studies have been done in both the gaseous and the liquid phases. The gaseous photochemical studies were performed by Cox and Atkins in 1973.<sup>4</sup> They used 330 to 380 nm light and as a result of their work they proposed two primary photodissociations shown in equations 14 and 15:

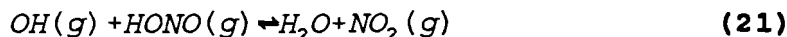
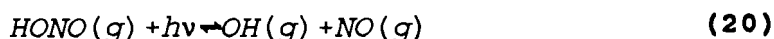


Cox and Atkins showed that the total primary quantum yield for these two dissociations is about one and they estimated that the yield for reaction 15 is half that of reaction 14. From this information, Cox<sup>12</sup> proposed a mechanism as follows:



From further studies, Cox concluded that reaction 15 contributes less than 10% to the overall reaction and that the primary quantum yield for reaction 14 is  $0.92 \pm 0.16$ .

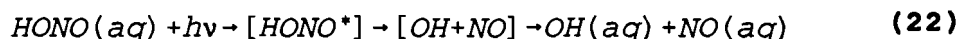
Nash proposed another gas phase photolysis based solely upon reaction 14 as the initiation step:<sup>13</sup>



No further mechanisms for nitrous acid gas phase photolysis have been suggested even though additional studies have been done.

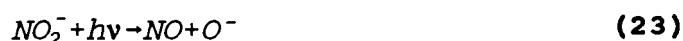
A few aqueous phase photochemical investigations have been performed. Murty and Dhar photolyzed solutions of nitrous acid at wavelengths greater than 445 nm and reported quantum yields up to 15.<sup>14</sup> However, these studies were performed above the region where nitrous acid absorbs readily (400-300 nm).

Rettich<sup>8</sup> suggested that the above decomposition was due to the thermal reaction produced by the heating of the light source. Accounting for factors such as ionic strength, pH, nitrite and nitrous acid concentrations, water source, light source, and reaction vessel geometry, Rettich studied the photochemistry of nitrous acid at 1°C. He discovered that the quantum yield for nitrous acid disappearance showed a linear increase from 0 at zero concentration to 0.14 at 0.14 M nitrous acid. However, for concentrations greater than 0.14 M the quantum yield remained constant at 0.14. Rettich also calculated the quantum yield of escape from the solvent cage as 0.095. The reaction of nitrous acid with the solvent cage is as follows:



The significant recombination of the hydroxyl radical and nitric oxide within the solvent cage is responsible for the low primary quantum yield.<sup>8</sup>

Since nitrous acid is in equilibrium with nitrite ion, if nitrous acid is of interest then by inference the reactions of nitrite ion may also be important. Holmes determined in 1926 that nitrite ion undergoes no net photolysis in aqueous solution.<sup>15</sup> This result was also confirmed later by Treinin and Hayon<sup>16</sup> in 1970 using a cadmium lamp(228.8 nm). This reaction is believed to occur by the following primary process:



which is analogous to the photochemical reaction of organic nitrites. They proposed the following mechanism under conditions of air saturated solutions with the presence of bromide and carbonate ions:



The bromide and carbonate ions then react with the hydroxyl radical produced in reaction 25 in the manner below:



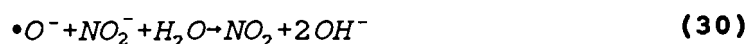
and



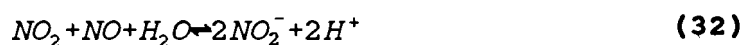
These mechanisms are possible due to the fact that spectra indicate the presence

of the transitory radical species,  $\text{Br}_2^-$  and  $\text{CO}_3^-$ .

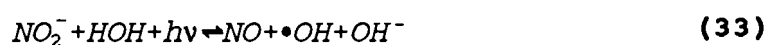
The  $\bullet\text{O}^-$  and  $\bullet\text{OH}$  radicals produced in reactions 24 and 25 can further react with additional nitrite ion in solution or with oxygen gas ( $\text{O}_2$ ) present in the air saturated solutions:



The absence of net photolysis of nitrite ion is attributed to the presence of efficient back reactions.<sup>15</sup> These reactions include the hydrolysis of several possible nitrogen oxide products from reactions 24, 29, and 30. According to Treinin and Hayon, the overall stoichiometry is

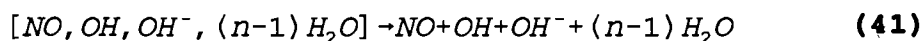
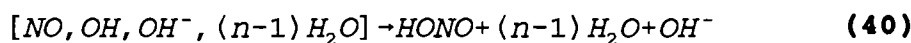
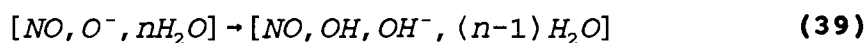
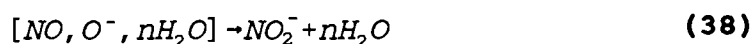
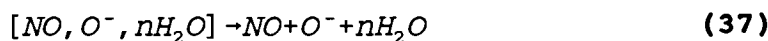


Contrary to its nonreactivity in aqueous solution, nitrite ion does show net photolysis in natural (sea) water. In 1981, Zafiriou and McFarland<sup>17</sup> reported that nitrite exhibited the following photolysis with sunlight:



Zafiriou and Bonneau<sup>18</sup> have since calculated the quantum yield of the reaction in terms of the production of hydroxyl radical. They discovered that the quantum yield was dependent upon wavelength and temperature but independent of pH, trapping agent,  $\text{O}_2$  pressure, and ionic strength.

The following mechanism was proposed by Zafiriou for the net photolysis of nitrite where the square brackets indicate species within the solvent cage:<sup>18</sup>



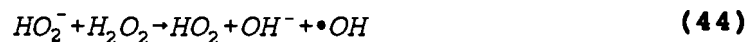
The quantum yield for the loss of nitrite varied from 2 to 27% per day for different water samples studied. This variation was attributed to 1) sensitized photolysis, 2) direct photolysis with a quantum yield sensitive to pH, oxygen concentration, salinity, temperature, and wavelength, and 3) regeneration of nitrite by secondary reactions of NO.<sup>18</sup>

Hydroxyl radical is of key interest in the reactions of both nitrous acid and nitrite ion, therefore, its pathways of production and destruction are of importance. It is well known that hydrogen peroxide thermally decomposes to

form oxygen gas and water as shown in reaction 42:<sup>19</sup>



Abel proposed a mechanism for the above reaction as follows:<sup>20</sup>

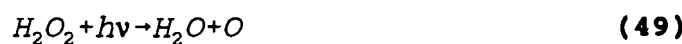


Hydrogen peroxide forms hydroxyl radicals in the presence of both light and a metal catalyst. In 1952, Hunt and Taube suggested two possible mechanisms for the photochemical dissociation of  $H_2O_2$ :<sup>21</sup>

Scheme I:



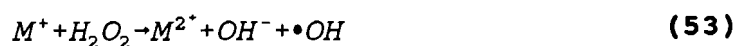
Scheme II:





Mansour<sup>22</sup> discovered that the decomposition of hydrogen peroxide was linear with respect to time of photolysis in a general experiment performed with benzene in sunlight. He noted that the decomposition increased with lower pH and high levels of water impurities, particularly metal ions.

In 1934, Haber characterized the decomposition of  $H_2O_2$  in the presence of a metal catalyst.<sup>23</sup> He proposed the following mechanism:

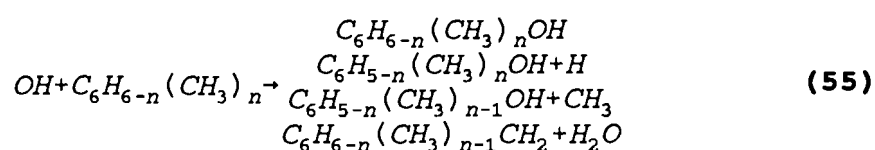


Ferric and cupric ions are the most commonly used catalysts for hydroxyl radical production.

Unlike nitrous acid, hydroxyl radical cannot be determined using standard ultra-violet spectrophotometry. Two reasons are: 1)  $\bullet OH$  is a transient species and is unstable in solution and 2)  $\bullet OH$  only absorbs in the vacuum UV region, below 200 nm.<sup>24</sup> The presence of hydroxyl radical is therefore detected by its reaction with scavengers such as aromatic or unsaturated organic compounds. The electron rich  $\pi$  bond is homolytically attacked by the hydroxyl radical to produce a new radical. If the double bond is part of an aromatic compound like benzene or toluene, then the resulting radical is more stable (than  $\bullet OH$ ) due to the stabilization from resonance forms.<sup>19</sup>

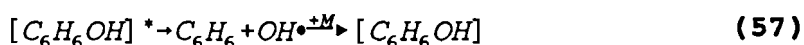
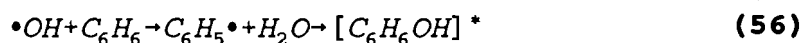


As with the reactions of nitrous acid, the gas phase scavenger reactions of hydroxyl radical have been the most widely investigated. In 1975, Davis *et al.* reported that the hydroxyl radical addition to benzene and toluene was pressure dependent, but no product analysis was performed.<sup>25</sup> Sloane characterized the addition of •OH to 1,3,5-trimethylbenzene, toluene, and benzene in 1978.<sup>26</sup> He found the following products:



where  $n = 0, 1, 3$

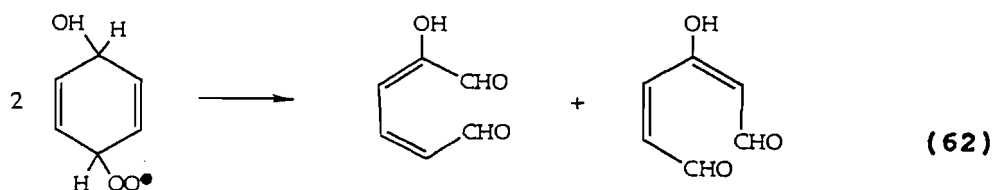
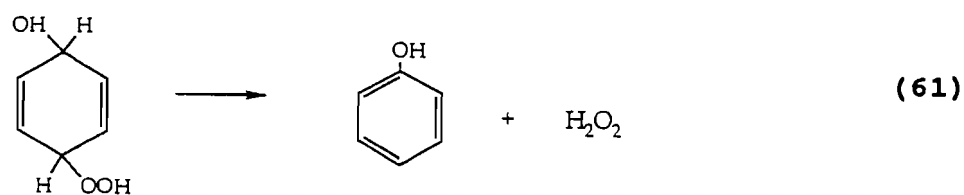
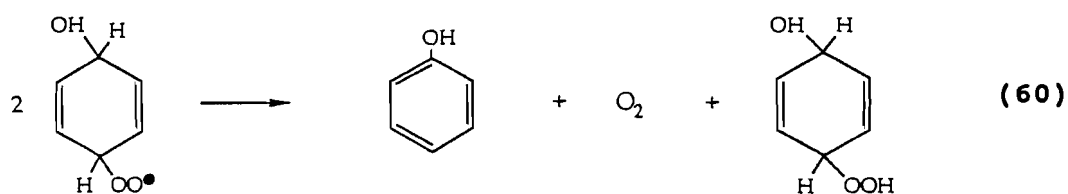
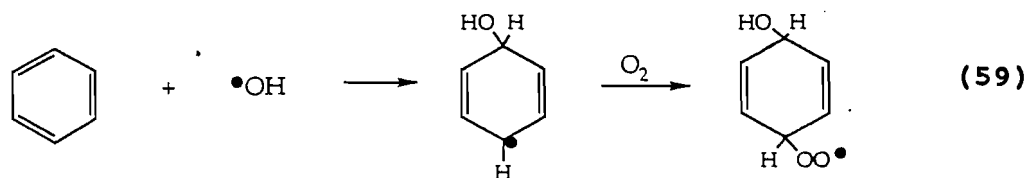
The temperature dependence of the radical addition to aromatic compounds was examined by Perry *et al.*<sup>27</sup> From this work the following reversible mechanism was proposed:<sup>28</sup>



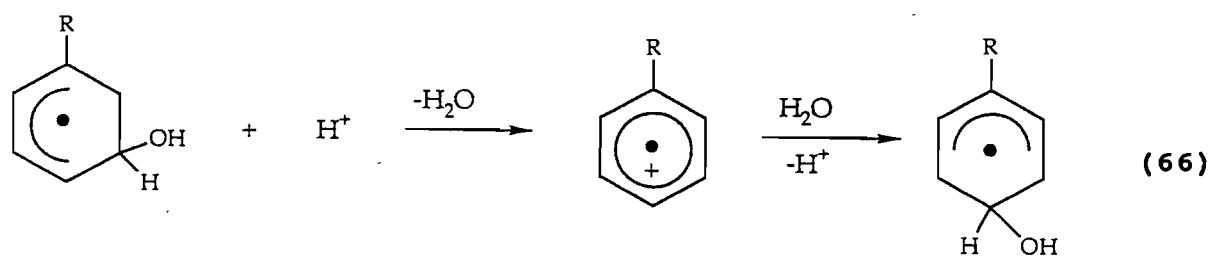
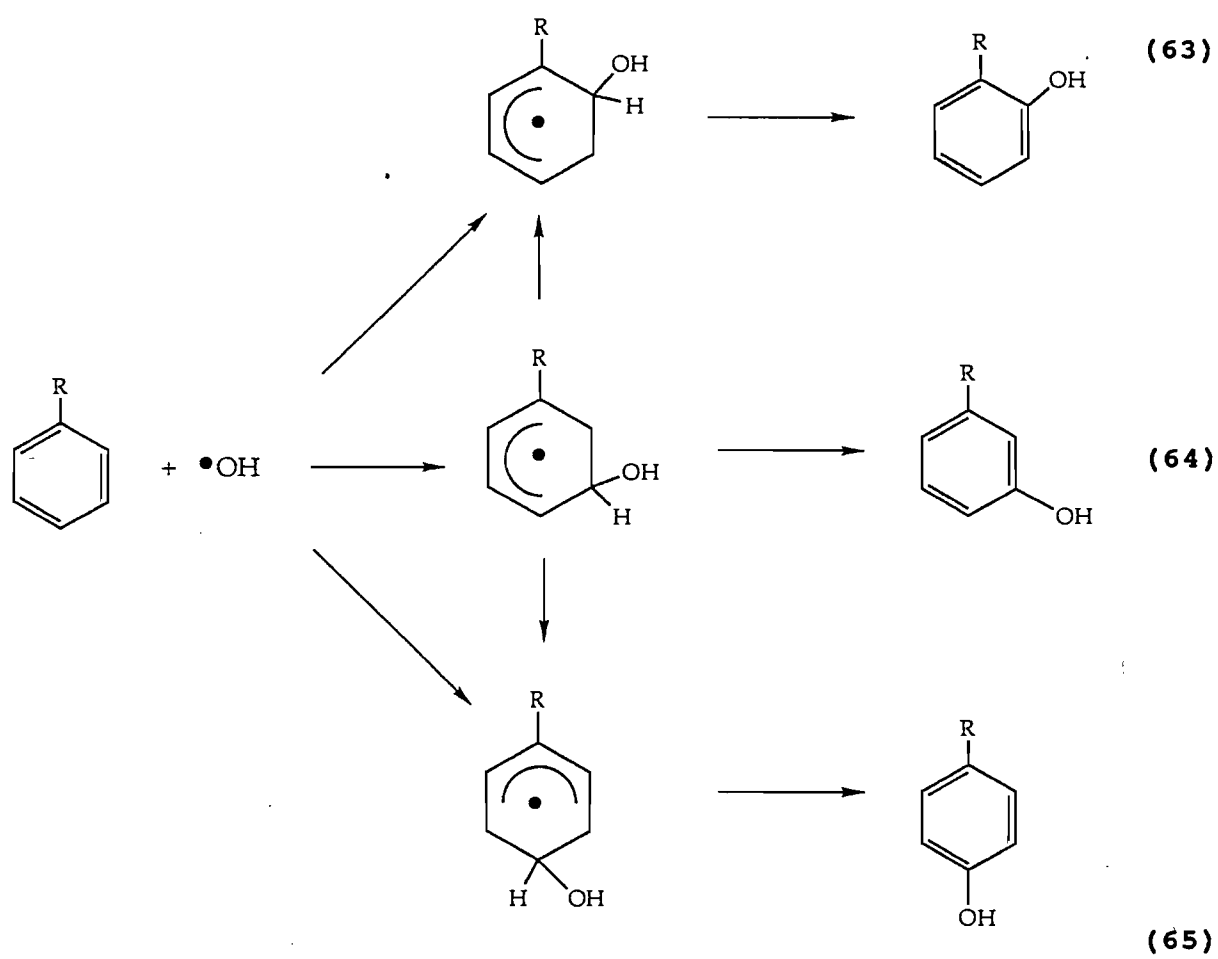
The products of the radical addition of •OH to aromatic compounds like benzene and toluene are phenol and para-nitrosophenol, (PNP). PNP is produced by the further reaction of phenol with nitrous acid.

The first mechanism for the reaction of aqueous benzene and hydroxyl radicals produced from H<sub>2</sub>O<sub>2</sub> was suggested by Jacob *et al.*<sup>29</sup> The products include

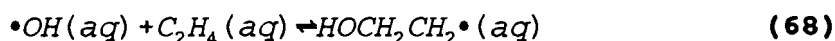
phenol,  $\alpha$ - and  $\beta$ -hydroxymuconaldehyde, and hydrogen peroxide.



Eberhardt investigated the hydroxylation mechanism for monosubstituted aromatics.<sup>30</sup>

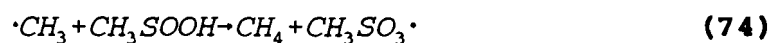
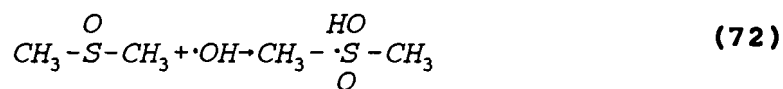


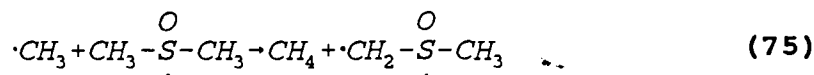
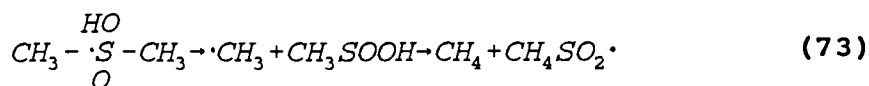
In his work with nitrous acid, Rettich employed ethylene and benzene as hydroxyl radical scavengers.<sup>8</sup> The mechanism for ethylene is shown in equations 67-71:



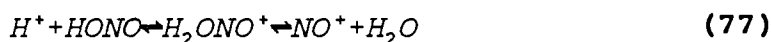
Glycoaldehyde, the product, decreased in concentration as the concentration of nitrous acid was increased. This trend was ascribed to an increase in competition with ethylene for hydroxyl radical.<sup>8</sup>

Dimethylsulfoxide, DMSO, is useful as an hydroxyl radical probe in biological systems.<sup>31</sup> Norman *et al.* were the first to study  $\bullet OH$  reaction with DMSO to give methyl radicals ( $\bullet CH_3$ ).<sup>32</sup> The proposed mechanism, deduced by ESR and radiolysis, is:

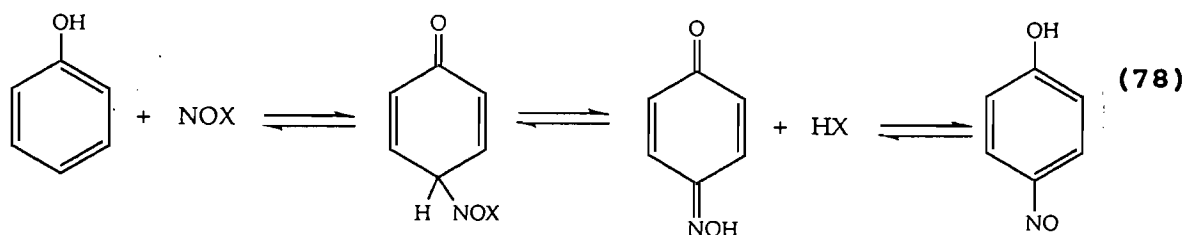




Challis *et al.* examined the kinetics and the mechanism for the nitrosation reaction of phenol.<sup>33,34</sup> It has been proposed that nitrous acid is in equilibrium with nitrosonium ion (NO<sup>+</sup>) in aqueous solution:<sup>35</sup>



Both the nitrosonium ion and its hydrated form can attack the aromatic ring of phenol to form p-nitrosophenol (PNP) by electrophilic substitution. Morrison proposed the following mechanism:<sup>35</sup>



Many studies indicate that nitrite ion undergoes no net photochemical reaction possibly due to efficient back reactions. Work done by Exstrom<sup>24</sup> with a

Blak-Ray B-100A low pressure mercury lamp did not show net nitrite photolysis. However, additional work by Johnson<sup>36</sup> with higher intensity mercury lamps suggests that, at least in the presence of a hydroxyl radical scavenger like benzene, nitrite displays an obvious photochemical reaction. The proposed products of this reaction are phenol and/or para-nitrosophenol. Previous work by Rettich<sup>8</sup> has indicated that pH does not affect the photochemical decomposition of nitrite. Zafiriou<sup>18</sup> has also stated that nitrite photolysis is independent of pH. More recent work by Hurd<sup>37</sup>, however, suggests that the reaction products' concentrations decrease at high pH.

The present study focusses on the photochemistry of nitrite ion in non-aqueous media. The use of aprotic organic solvents allows nitrite to be separated from nitrous acid and its photochemical properties examined independent of those for the conjugate acid. Aprotic solvents do not have the capability to donate a hydrogen ion and thus protonate the nitrite ion to form nitrous acid. Polar solvents are necessary to dissolve significant amounts of the inorganic salts of nitrite. Therefore, various polar, aprotic organic solvents were examined for their usefulness as solvents for the study of nitrite's photochemical properties. Similar work by Gibson<sup>38</sup> is in progress on the photochemistry of the molecular form in aromatic solvents.

## EXPERIMENTAL

### Apparatus:

The photochemical reactions were performed with a Rayonet photochemical reactor, model #RPR-100. The source of light for all reactions were sixteen mercury lamps banded at  $366 \pm 5$  nm. Solutions were photolyzed in 20 mL quartz reaction tubes for the times noted. Ultraviolet/visible absorbance measurements were taken with a Perkin-Elmer 559 UV-Vis spectrophotometer using a slit width of 1.0 nm and 1.000 cm quartz cells.

### Solvent Suitability Tests:

Solvent suitability tests were done by weighing out 0.02-0.03 g of  $\text{NaNO}_2$  (Merck, reagent grade) into a 10 mL volumetric flask and solvent was added to volume. If not all of the solid dissolved, the solution was allowed to reach saturation by sitting overnight. The solvents used were dimethylsulfoxide (anhydrous, Aldrich, Gold Label, 99+ %), 1,1-dimethoxyethane (Eastman, 99%), 1,2-dimethoxyethane (EM Science, 98%), p-dioxane (Eastman, Scintillation Grade), tetrahydrofuran (Fisher, Histological Grade), dimethylformamide (Baker, Analyzed reagent, 99.0%), and acetonitrile (Baker, Analyzed reagent, 99.5%). Ultraviolet-visible spectrophotometry was used to detect the presence of dissolved nitrite (anticipated  $\lambda_{\text{max}} = 365$  nm). In some cases, spectra indicated the formation of nitrous acid so an attempt was made to dry these solvents and run additional UV-visible spectra of dry solutions. Dimethylformamide was dried over anhydrous magnesium sulfate (Fisher, Certified grade) while 1,2-dimethoxyethane

was dried over anhydrous calcium hydride (Fisher, Purified grade). The p-dioxane was dried by reflux with fresh Na metal and benzophenone (Fisher, Certified grade) until the solution turned blue.

#### **Photolysis of nitrite ion in DMSO:**

A 10.0 mL aliquot of 1.0, 0.5, 0.25, or 0.12 M  $\text{NaNO}_2$  in DMSO was placed in a quartz reaction tube. Up to four reaction tubes could be placed in the merry-go-round apparatus within the Rayonet reactor and photolyzed at one time. Photolysis times were varied from 15 to 60 minutes. Ultraviolet/visible spectrophotometry was used to detect the disappearance of nitrite and the appearance of products.

#### **Thermolysis of DMSO and nitrite ion in DMSO:**

A 10.0 mL aliquot of 0.5 or 0.25 M  $\text{NaNO}_2$  in DMSO was placed in a 20 x 225 mm test tube. This solution was then bubbled with either  $\text{N}_2$  (Genex, Dry grade) or  $\text{O}_2$  (Genex) gas using a sparging stone for 5 minutes. The test tube was covered with a septum and the headspace was purged with  $\text{N}_2$  or  $\text{O}_2$  gas for 5 minutes. A similar procedure was followed for tubes of pure DMSO. The tubes were placed in a constant temperature bath held at 60°C for 60 minutes. To prevent problems due to the extreme heating, the tubes were vented to the atmosphere with 22 gauge needles. Ultraviolet/visible spectrophotometry was used to measure the changes, if any, due to thermolysis.

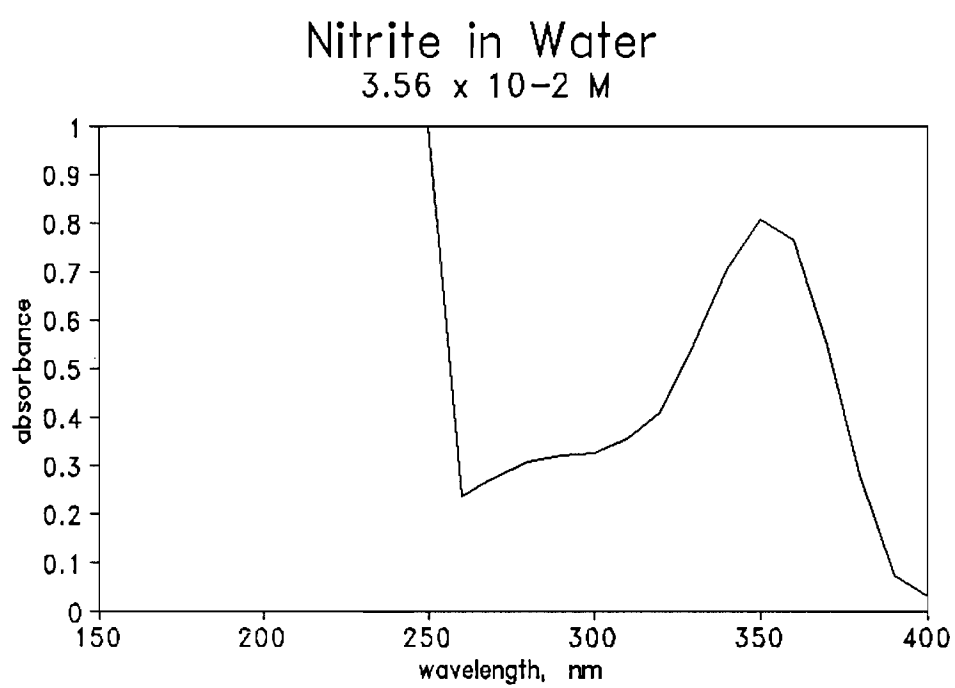


## RESULTS

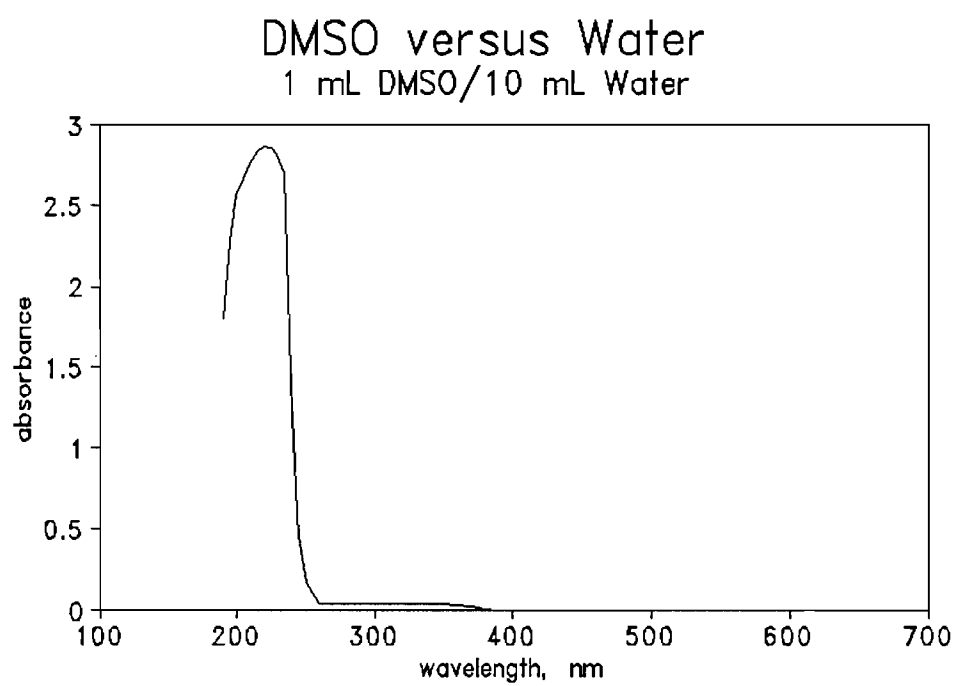
Table 1: Table of Solvent Properties

Solvent	Observations
Dimethyl sulfoxide	Good solubility, Clear nitrite peak
1,2-Dimethoxyethane	Acid peaks seen
p-Dioxane	Acid peaks seen
Tetrahydrofuran	Poor absorbance spectra
Acetonitrile	Poor solubility
Dimethylformamide	Acid peaks seen

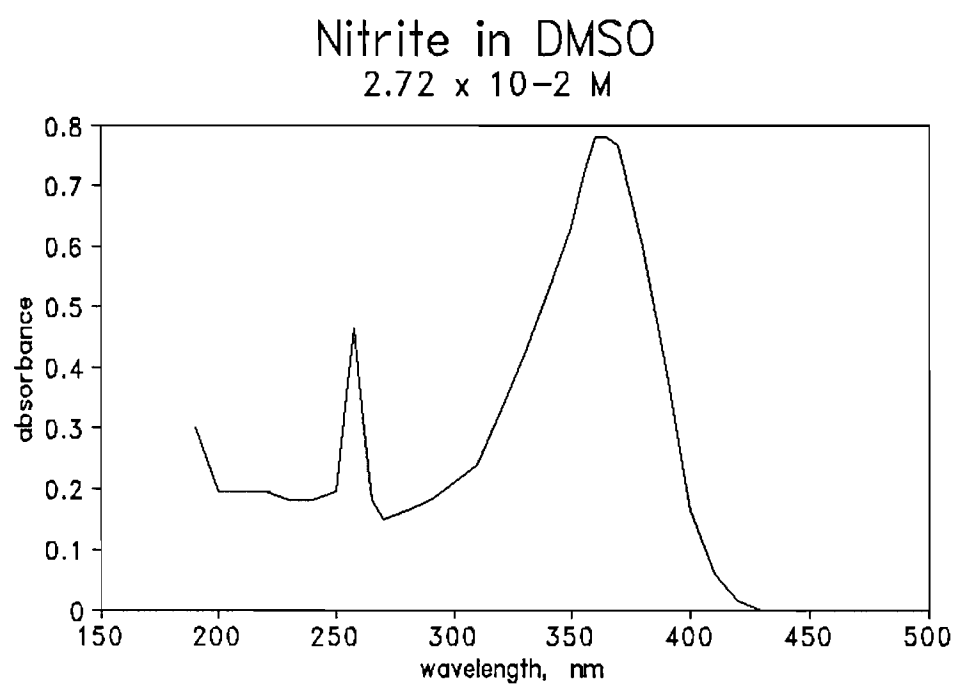
**Figure 1**



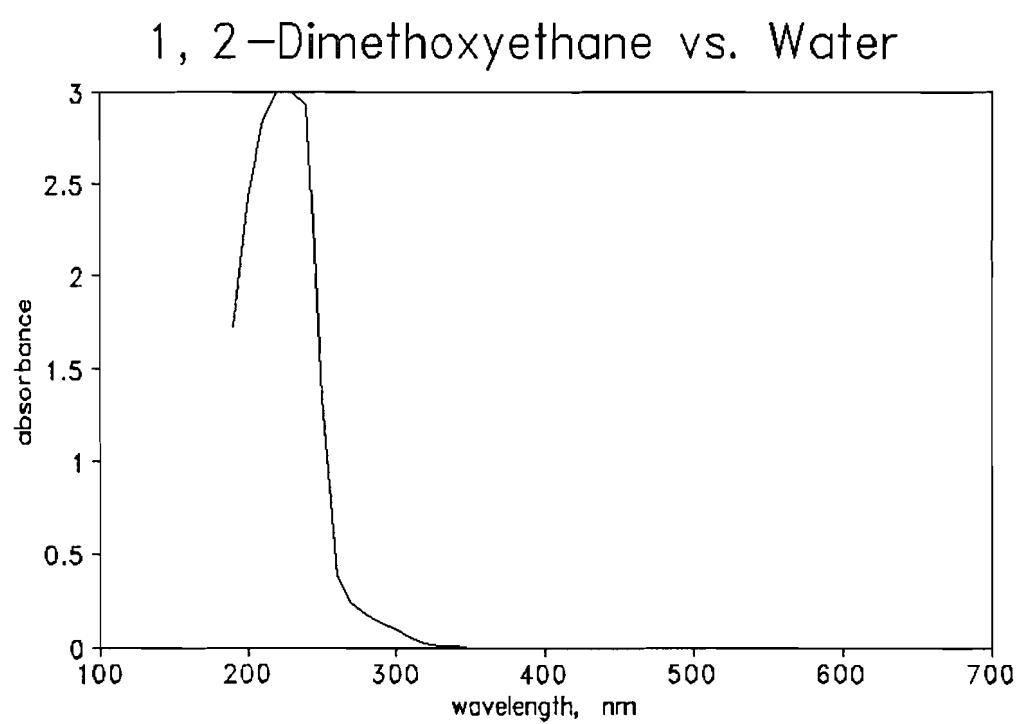
**Figure 2**



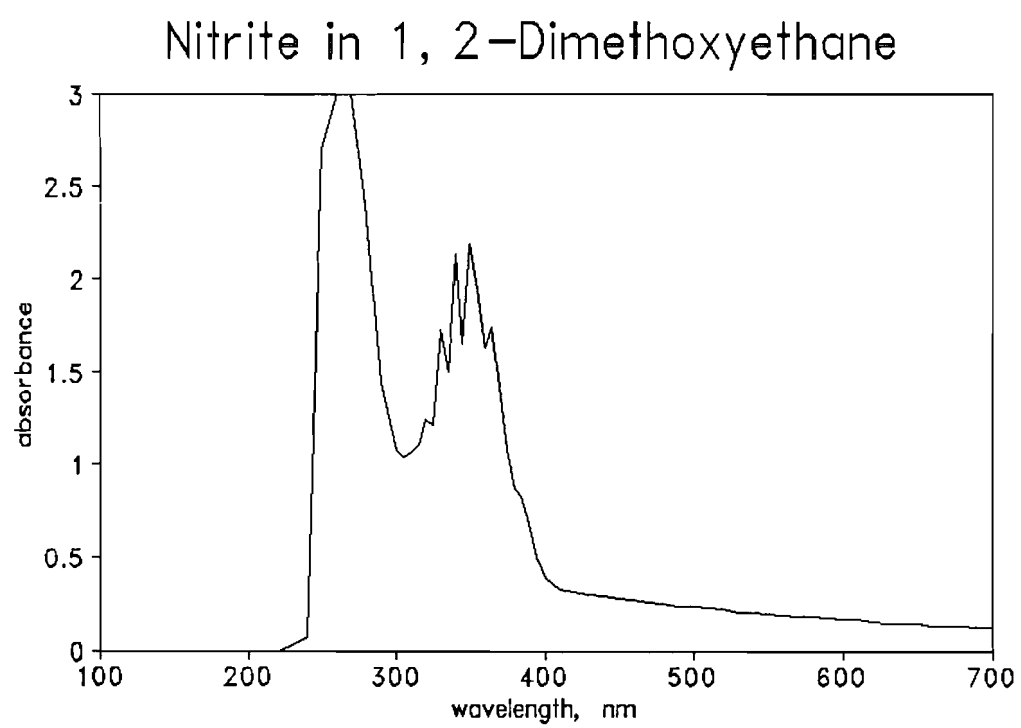
**Figure 3**



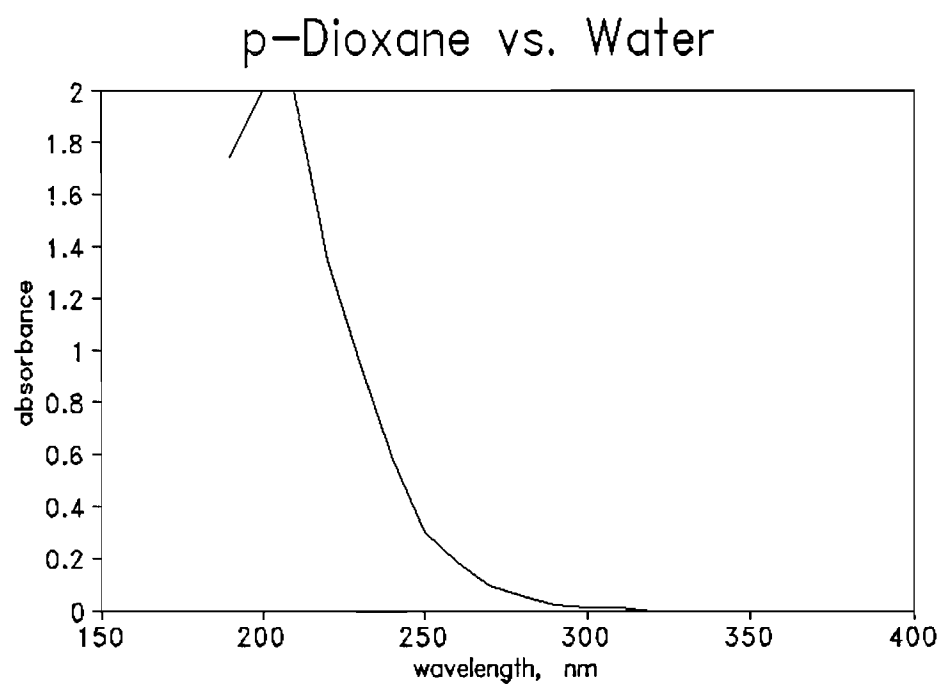
**Figure 4**



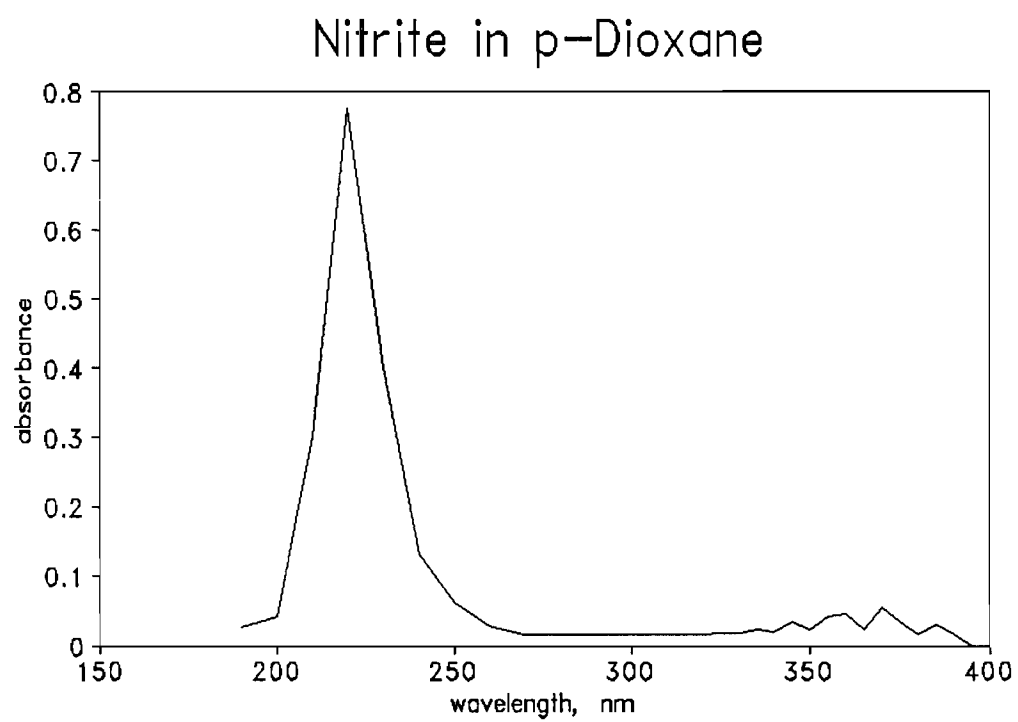
**Figure 5**



**Figure 6**

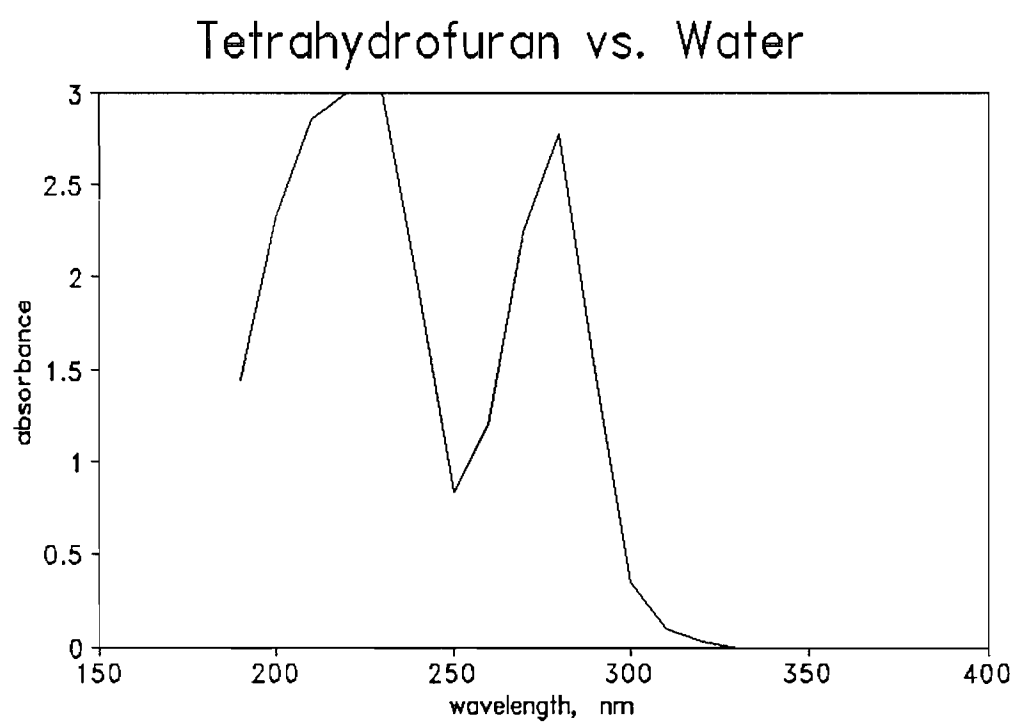


**Figure 7**

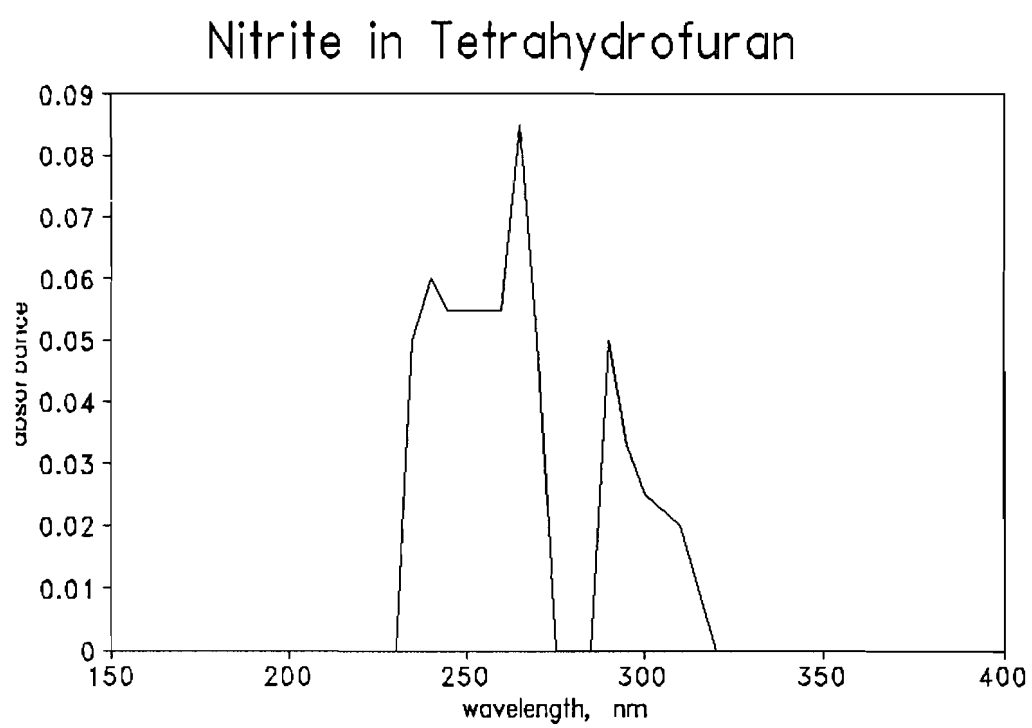




**Figure 8**



**Figure 9**



**Figure 10**

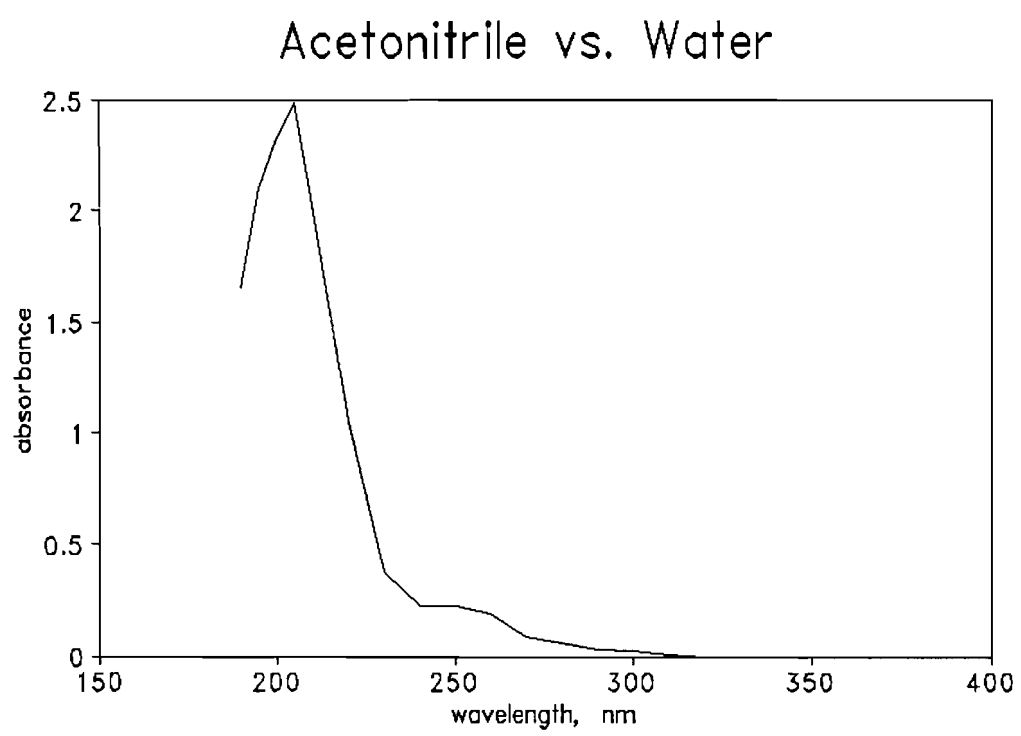
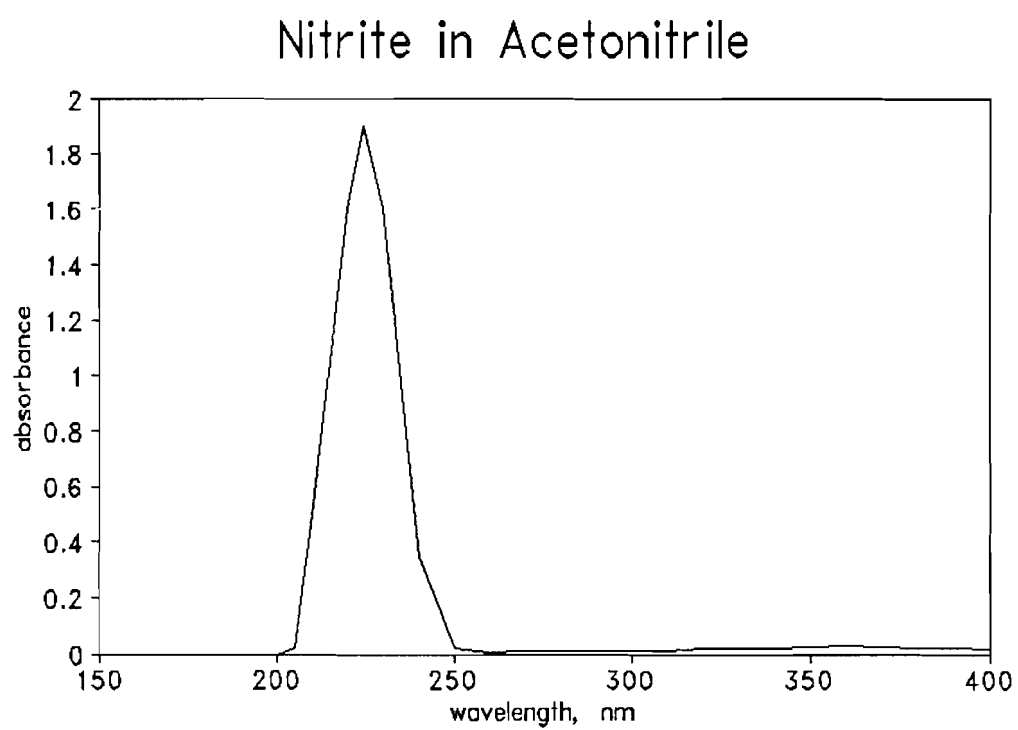
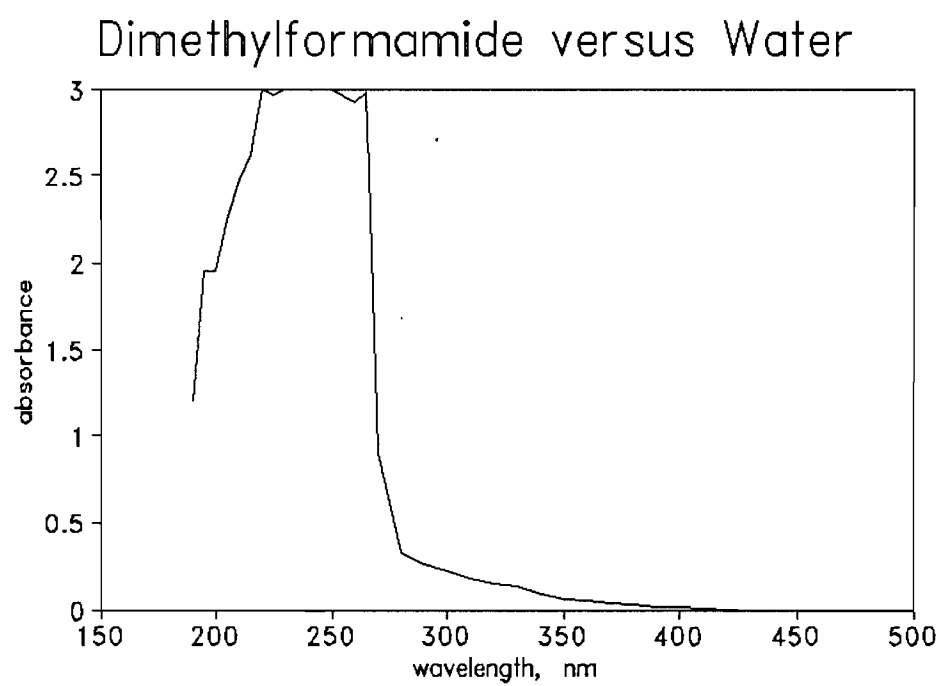


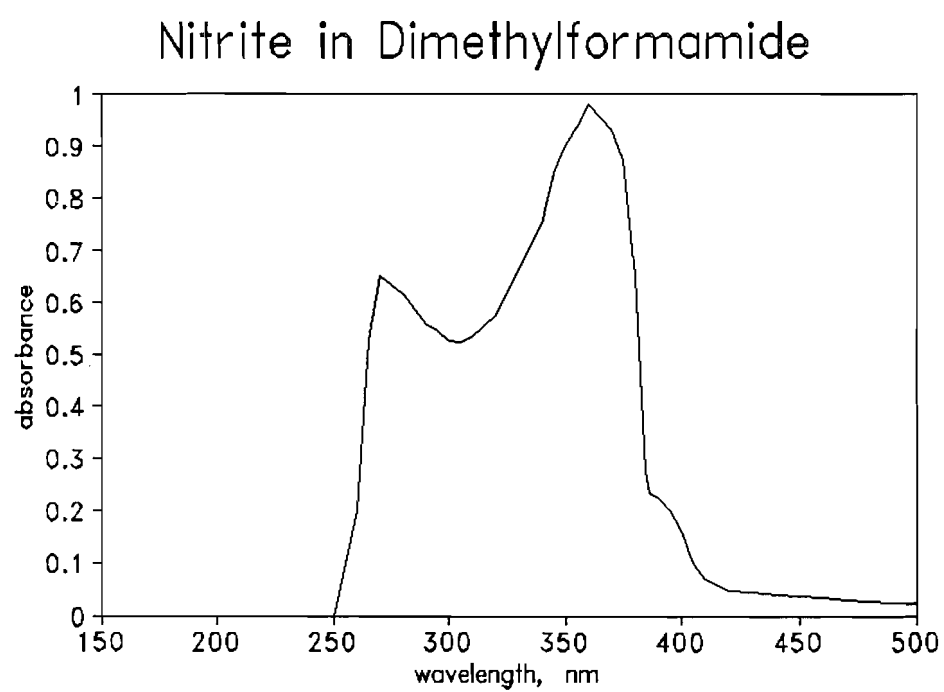
Figure 11



**Figure 12**



**Figure 13**



**Figure 14**

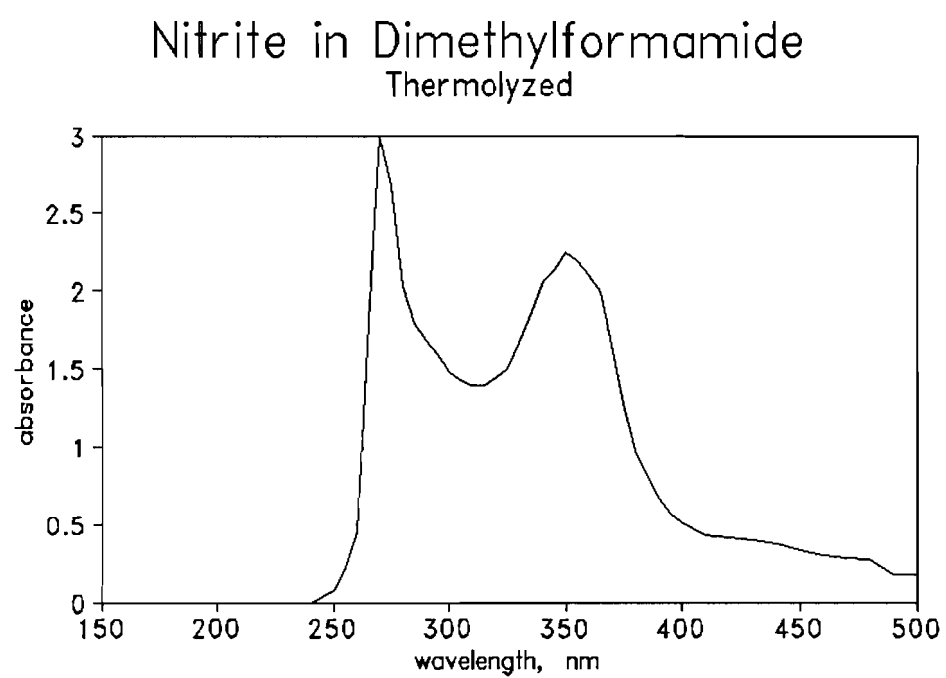


Figure 15

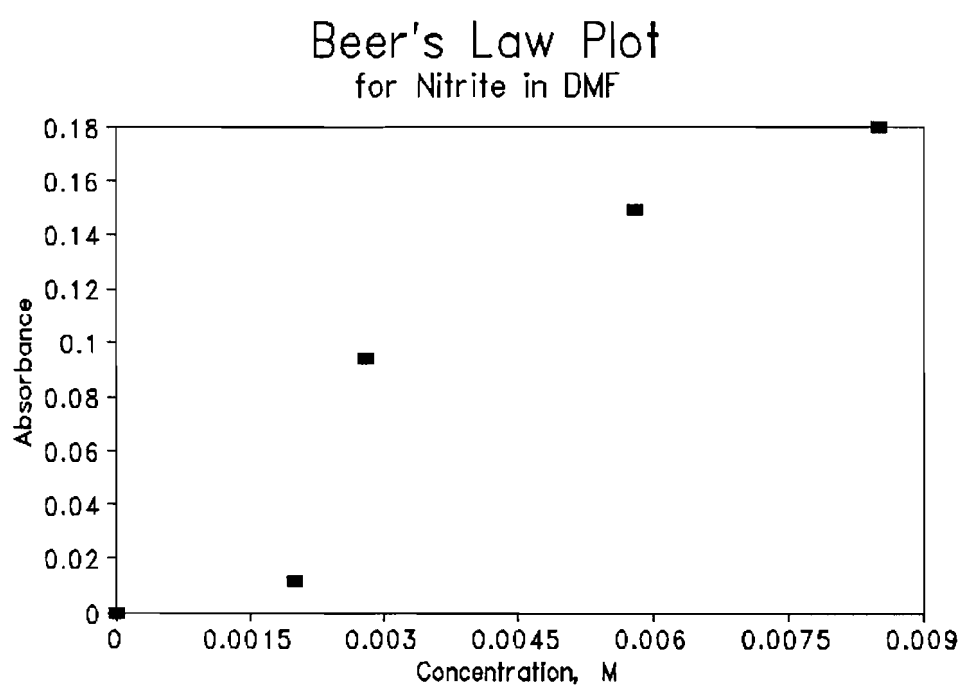




Figure 16

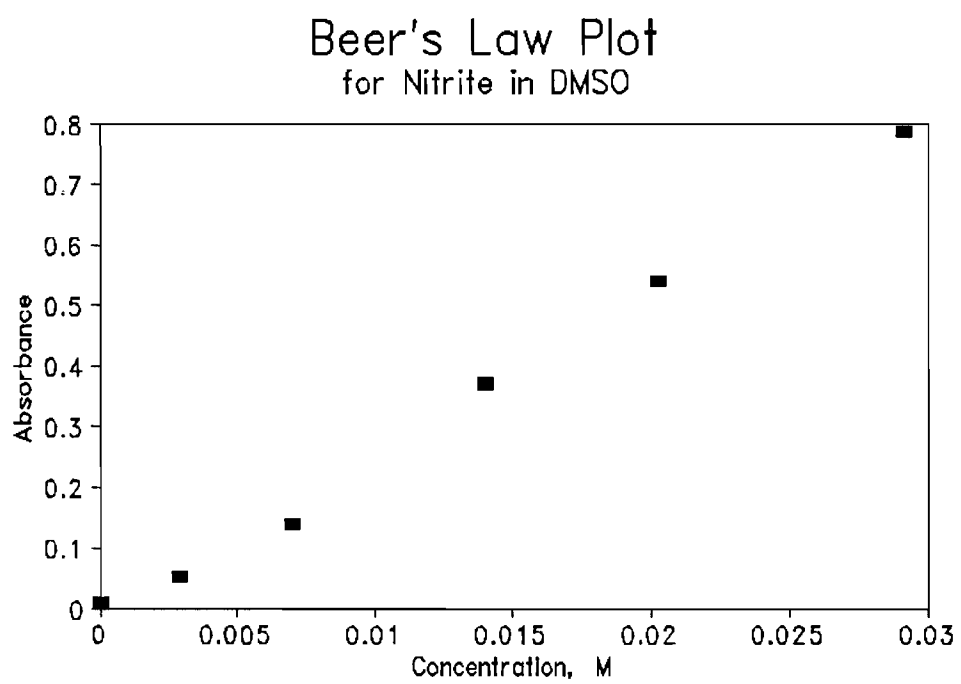
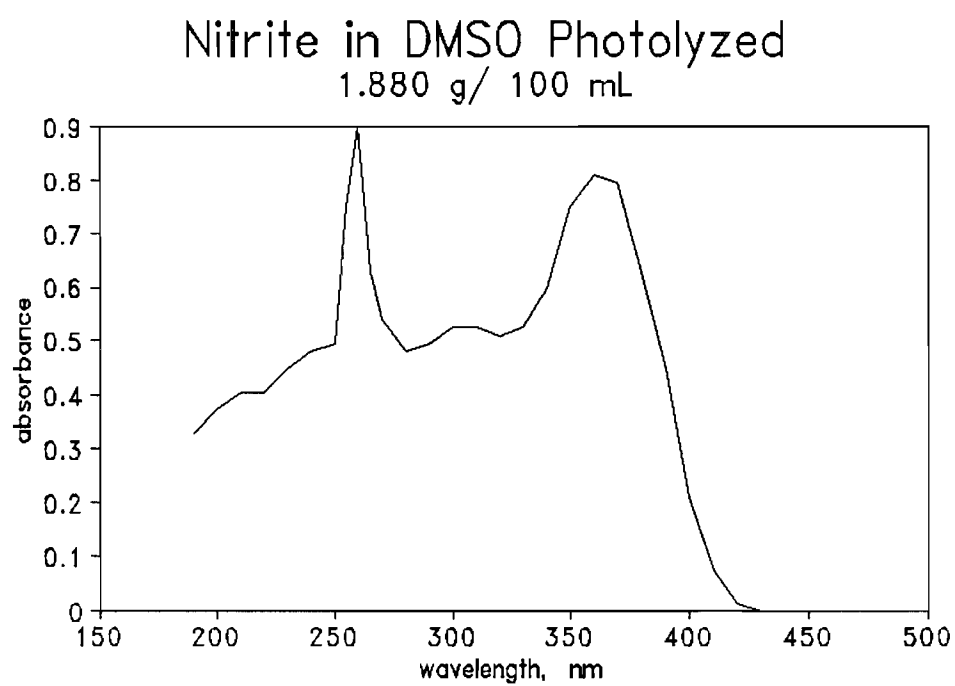
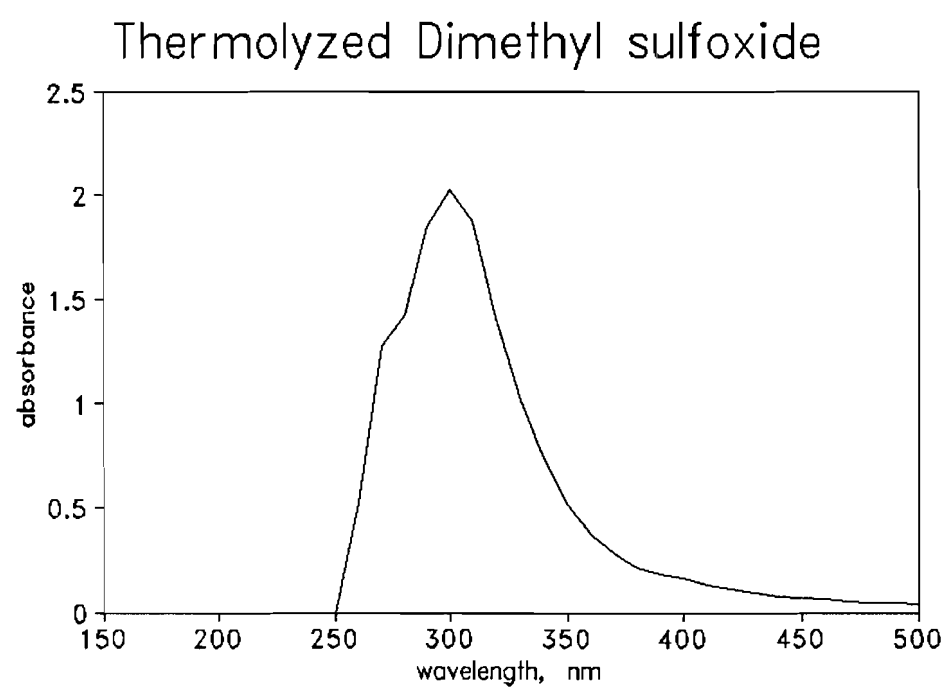


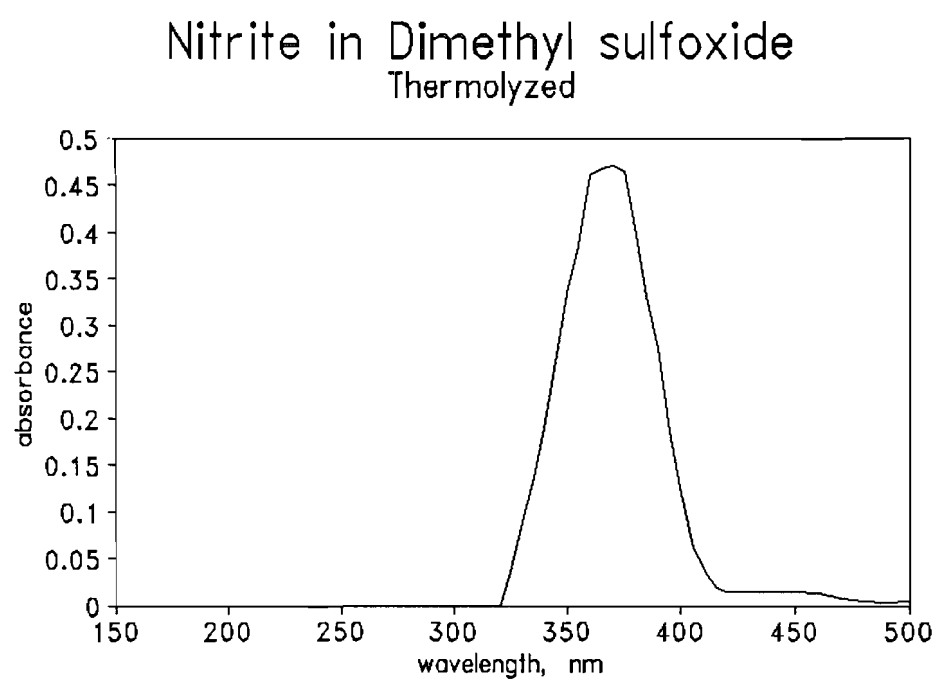
Figure 17



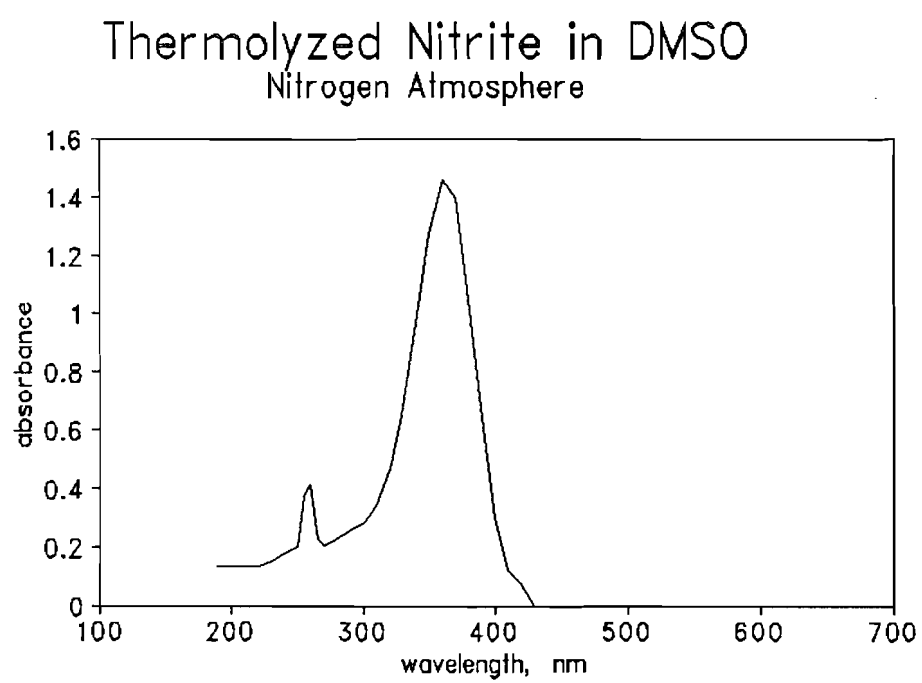
**Figure 18**



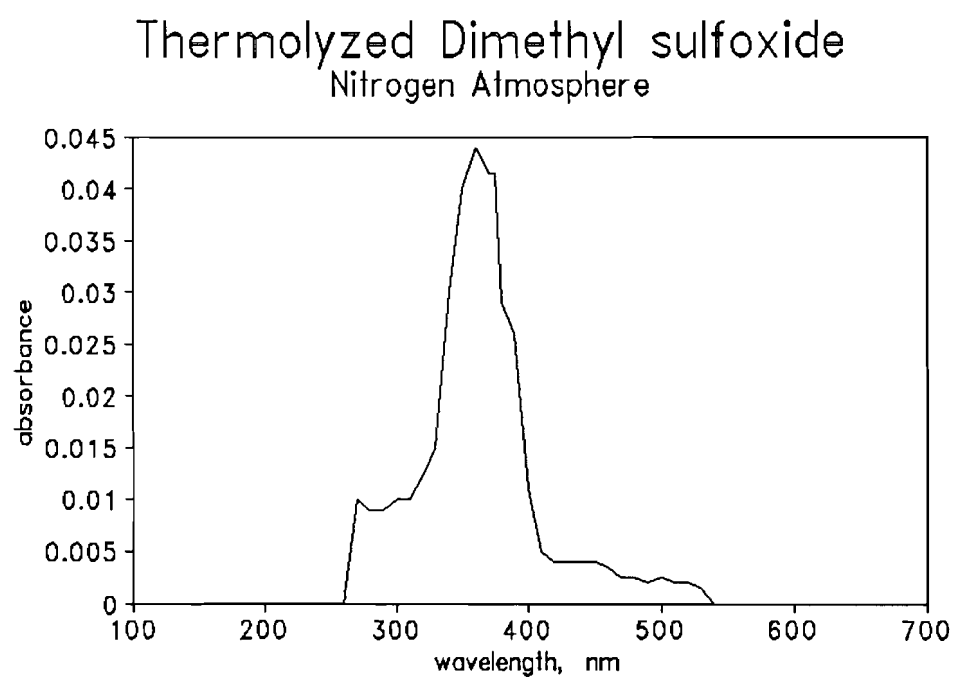
**Figure 19**



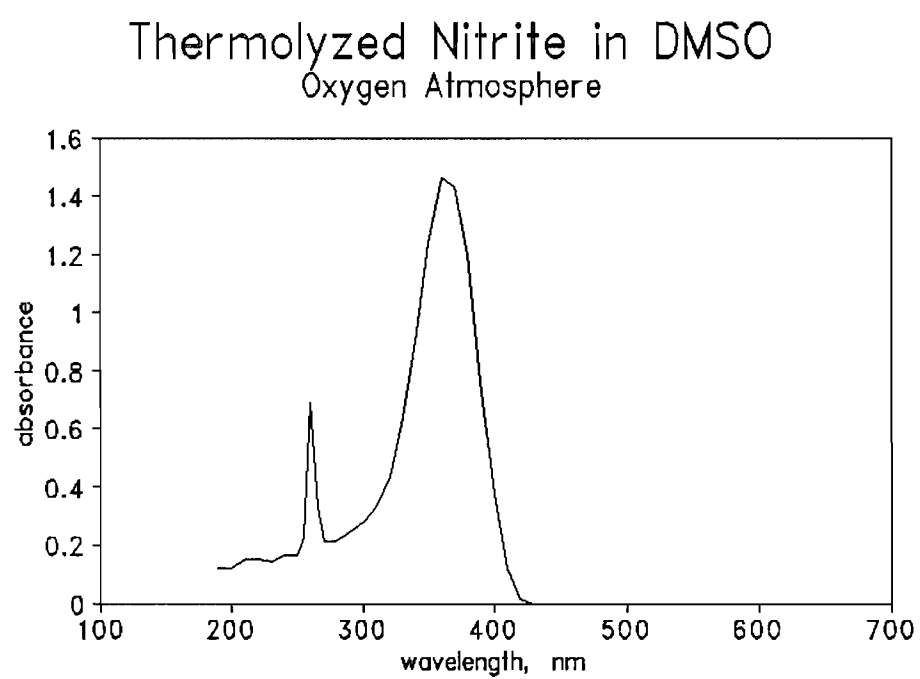
**Figure 20**



**Figure 21**



**Figure 22**



**Figure 23**

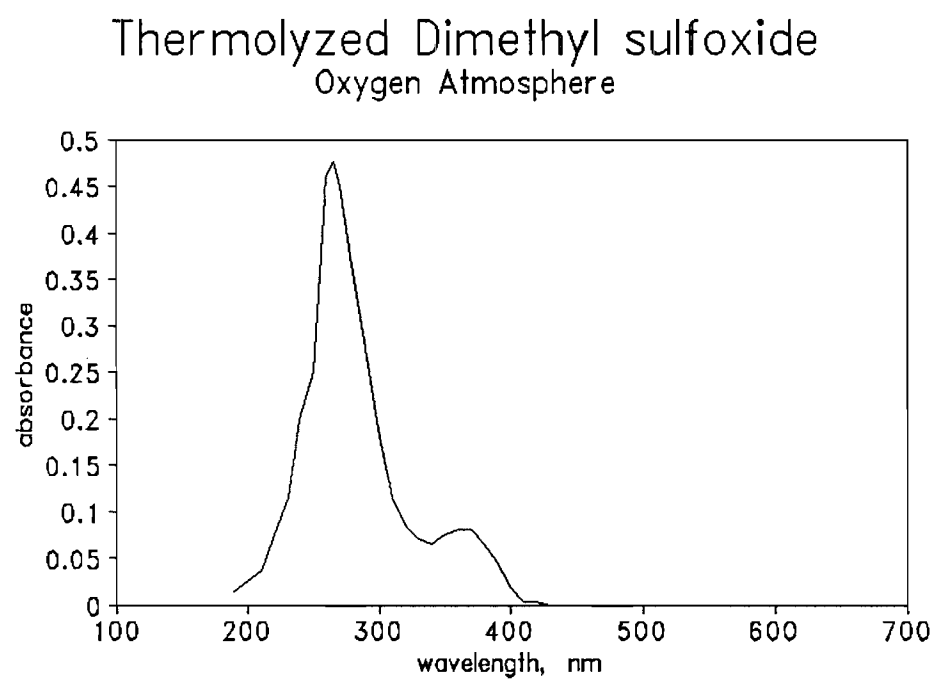




Table 2: Table of Beer's Law Data for Nitrite in DMF

Concentration, M	Absorbance @ 368.0 nm
0.0	0.000
2.0e-03	0.012
2.8e-03	0.094
5.8e-03	0.149
8.5e-03	0.180

Table 3: Table of Regression Data for DMF Beer's Law Plot

Regression Output:	
Constant	-9.8e-06
Std Err of Y Est	0.028924
R Squared	0.902477
No. of Observations	5
Degrees of Freedom	3
X Coefficient(s)	22.77743
Std Err of Coef.	4.322946

Table 4: Table of Beer's Law Data for Nitrite in DMSO

Concentration, M	Absorbance @ 364.0 nm
0.0	0.011
2.9e-03	0.052
7.0e-03	0.140
1.4e-02	0.371
2.0e-02	0.540
2.9e-02	0.787

Table 5: Table of Regression Data for DMSO Beer's Law Plot

Regression Output:	
Constant	-0.01916
Std Err of Y Est	0.023224
R Squared	0.995398
No. of Observations	6
Degrees of Freedom	4
X Coefficient(s)	27.50298
Std Err of Coef.	0.935076

## DISCUSSION

It is not possible to measure the quantum yield of the photochemical disappearance of nitrite ion in aqueous solution without the contributing complications of nitrous acid. Therefore, to determine the independent photochemistry of nitrite it is necessary to dissolve the nitrite salt in aprotic organic solvents. Several organic solvents were tested for their suitability including dimethylsulfoxide, 1,1-dimethoxyethane, 1,2-dimethoxyethane, p-dioxane, tetrahydrofuran, acetonitrile, and dimethylformamide. These solvents also had to exhibit significant polarity in order to dissolve the ionic sodium nitrite salt. Dimethyl sulfoxide (DMSO) was the first solvent to be used. The entire amount of salt dissolved and the ultraviolet-visible spectrum displayed the peak for dissolved nitrite ( $\lambda_{\text{max}} = 365 \text{ nm}$ ) with no sign of the five "finger-like" peaks of HONO in the region of 350-400 nm (Figure 3). DMSO also did not show significant absorbance versus water until 250-190 nm (Figure 2).

1,1-dimethoxyethane did not appear to dissolve any of the sodium nitrite. The UV-visible spectrum for the solvent versus solvent contained large peaks, so 1,1-dimethoxyethane was discarded as a reasonable solvent. It was thought that the solubility of nitrite would be improved with 1,2-dimethoxyethane and it was (Figure 5). The solvent versus water spectrum had significant absorbance in the 260-190 nm region and some as high as 310nm. The spectrum of nitrite indicated the presence of the molecular form (Figure 4). The 1,2-dimethoxyethane was then dried to see if the acid form was due to moisture present in the reagent

solvent. Unfortunately, the acid peaks were still present in the dried solution's spectrum, so it was concluded that the solvent either picked up water very quickly from the air or nitrite was able to remove some of the protons from the solvent molecule.

The next solvent to be tried was p-dioxane. The solvent versus water spectrum had a significant absorbance in the area of 190 to 300 nm (Figure 6). The spectrum of saturated sodium nitrite in p-dioxane exhibited the distinct "fingers" of the molecular form (Figure 7). The p-dioxane was dried by distillation over Na metal in the presence of benzophenone. The blue color of the solution when it was dry disappeared rapidly when the solution was exposed to the atmosphere, so p-dioxane was eliminated as a possible solvent for nitrite photolysis.

Tetrahydrofuran (THF) also did not readily dissolve the entire sample of nitrite. The solvent absorbs in the region 190-280 nm versus water (Figure 8). When the THF solvent versus solvent spectrum was taken, it showed absorbances greater than that of the saturated nitrite in THF (Figure 9). Therefore, tetrahydrofuran is not an appropriate solvent for the nitrite.

Nitrite had an extremely low solubility in acetonitrile. Again, the solvent versus water absorbed more strongly than the nitrite solution (Figures 10 & 11). The only possible evidence of dissolved nitrite is a small absorbance (0.03 Aunits) in the region of 320-400 nm. Thus due to poor solubility, acetonitrile was discarded as a possibility for the nitrite solvent of choice.

Dimethylformamide samples were dried over magnesium sulfate before being used to dissolve the sodium nitrite. The solvent versus water spectrum (Figure 12) shows that DMF absorbs significantly in the region from 190-280 nm and some absorbance occurs in the area of nitrite's  $\lambda_{\text{max}}$ . Comparison of the spectra of both "wet" (straight from the bottle) and dry solvents shows them to be quite similar. The solvent versus solvent spectrum (A24) has an interesting absorbance in the region 250-260 nm, however this was corrected in A25. Nitrite seems to have a broad absorbance in DMF from 260-400 nm; it is a large peak at 360 nm with a wide shoulder at 280 nm (Figure 13). Another spectrum of the same solution of saturated nitrite in DMF was taken at a later time to see if the absorbance pattern changed with time. Unfortunately, the solution did not seem to be thermally stable because the spectrum did change; the shoulder at 280 nm became more pronounced and a slight shoulder appeared at 390-400 nm. The absorbance values for saturated nitrite in wet DMF (A29) were significantly lower than those of the corresponding "dry" solution. A Beer's law plot was prepared (Figure 15); it had a least squares correlation value of 0.90 (Table 3). A thermolysis was performed with both solvent and nitrite in DMF to test the thermal stability of the solutions. Spectrum A28 is the nitrite solution before thermolysis and A35 is the same solution after thermolysis. Thermolysis resulted in significant spectral changes (Figure 14). The peak at 270 nm grew to be larger than the peak at 350 nm but all of the absorbance values increased as evidenced in the necessary change of the scale maximum from 1 absorbance unit to 3 Aunits.

Similar effects were seen with "wet" solvent but a change of scale maximum was not required. The effect of thermolysis on the spectrum of dimethylformamide versus water is a change of shape in the 240 nm peak; it falls and rises differently at the beginning and end of the peak (A37 & A38). Finally, sodium nitrate was dissolved in DMF as comparison for nitrite to see the effects of thermolysis. Saturated nitrate in DMF had a  $\lambda_{\text{max}}$  of 310 nm (A39). Thermolysis of the nitrate solution resulted in a significant growth at 270 nm, very near the region of growth in the nitrite spectra (A40).

From all of the above information, dimethyl sulfoxide was chosen as the best solvent to study the photochemical and thermal reactions of nitrite ion. Spectra A41 through A45 are for the Beer's law plot of nitrite in DMSO. The least squares regression correlation is 0.995 (Table 4). Before photolysis, UV-visible spectra were taken of the four concentrations of nitrite in DMSO from 0.125 to 1.00 M (A48-A51). The solutions were photolyzed for 60 minutes with 365 nm light. There did not appear to be any volume change with photolysis, so any concentration change was not due to solvent evaporation. There was, however, a significant change in temperature from 28°C to 60°C due to the heat produced by the photolysis lamps. Spectra A52 to A56 are from DMSO samples that were photolyzed for varying times. DMSO does not absorb at 365 nm so no photolysis reaction could occur. Thus, these spectra show the effect of the lamp heating on the solvent. DMSO must undergo some type of thermal reaction as evidenced by the growth with time of the peak at 260 nm. Spectra A57 to A64

show the changes in the nitrite-DMSO solution upon photolysis. There is a peak growing in at 300 nm in between the two peaks of the solutions before photolysis. This peak is more obvious in the lower concentrations; it seems to be overwhelmed by the peak at 350 nm.

Since there was significant heating of the photolysis solutions, it was necessary to investigate the possibility that the results were due to a thermal process rather than the light. Spectra A65 and A66 are of thermolyzed DMSO versus non-thermolyzed DMSO; there is a large absorbance in the region of 260-400 nm. The spectra of nitrite in DMSO did not appear to change significantly upon thermolysis, but a small peak at 440 nm was seen when the maximum scale was changed to 1 Aunit (A67-A68). The thermolyzed solutions of nitrite in DMSO were bubbled with nitrogen gas to determine if any of the thermolysis products were dissolved gases. The spectra remained unaltered after purging with  $N_2$  (A69-A70). The effect of different gases on the thermal reaction of both DMSO and nitrite in DMSO was studied. Solutions were bubbled with either nitrogen or oxygen gas for several minutes and then they were capped. The thermolysis was performed under conditions similar to those that occur in photolysis; the solutions were heated for 60 minutes at the peak temperature of photolysis, 60°C. The thermolyzed DMSO in the nitrogen environment (A71 and A72) seemed to show an absorbance at 365 nm, where nitrite absorbs. It seems probable that that particular peak is due to contamination. The thermolyzed nitrite in DMSO under nitrogen appeared unchanged except for the shoulder

developing at 420 nm (A73 and A74). The thermolyzed DMSO in an oxygen environment showed a peak at 365 nm, where nitrite's  $\lambda_{\max}$  is, perhaps due to contamination (A75). The thermolyzed nitrite in DMSO under oxygen conditions displayed no obvious sign of thermolysis; there were only the same two peaks seen in the unthermolyzed solution.

The effects of thermolysis and photolysis on the nitrite in DMSO system are still not fully understood. It is not clearly indicated whether or not the products in the photolysis spectrum are due to the influence of light or perhaps partially due to the heating from the light source. The thermolysis study was rather inconclusive since there is some question as to the reliability of the results. Therefore, more careful work needs to be done to prevent possible contaminants. Another feasible method to study the effect of photolysis alone is to cool the sample as it is being photolyzed with an antifreeze bath to counteract the effect of source heating. One could also use a lower intensity source that would produce significantly less heat. Work still needs to be done in the area of product separation and identification for both heat and light induced phenomena.



## FUTURE RESEARCH

Future research could concentrate on the continued study of the thermal reaction of  $\text{NO}_2^-$  in dimethylsulfoxide. Further work also needs to be done on the photochemical reaction of nitrite in DMSO. Specifically, the effect of controlled amounts of water on the photolysis of nitrite and the effect of controlled amounts of water in the presence of hydroxyl radical scavengers on nitrite photolysis. Also, the identification of the photolysis products from both the molecular and ionic forms needs to be addressed.

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Appendix of Spectra  
Kathryn E. Shanks  
Honors Research Paper  
May, 1993

## Appendix of Spectra

1. Nitrite in water ( $3.56 \times 10^{-2}$ M) . . . . .	A1
2. Nitrite in dimethyl sulfoxide ( $3.41 \times 10^{-2}$ M) . . . . .	A2
3. Dimethyl sulfoxide versus water . . . . .	A3
4. Dimethyl sulfoxide in water versus water . . . . .	A4
5. Dimethyl sulfoxide versus water II . . . . .	A5
6. Dimethyl sulfoxide in water versus water II . . . . .	A6
7. 1,2-Dimethoxyethane versus water . . . . .	A7
8. Saturated nitrite in 1,2-dimethoxyethane . . . . .	A8
9. Saturated nitrite in dry 1,2-dimethoxyethane (0-1) . . . . .	A9
10. Saturated nitrite in dry 1,2-dimethoxyethane (0-3) . . . . .	A10
11. p-Dioxane versus water . . . . .	A11
12. Saturated nitrite in p-dioxane . . . . .	A12
13. Tetrahydrofuran versus water . . . . .	A13
14. Saturated nitrite in tetrahydrofuran . . . . .	A14
15. Nitrite in THF/solvent vs. solvent . . . . .	A15
16. Acetonitrile versus water . . . . .	A16
17. Saturated nitrite in acetonitrile . . . . .	A17
18. Dimethylformamide versus water . . . . .	A18
19. Dry dimethylformamide versus water (0-1) . . . . .	A19
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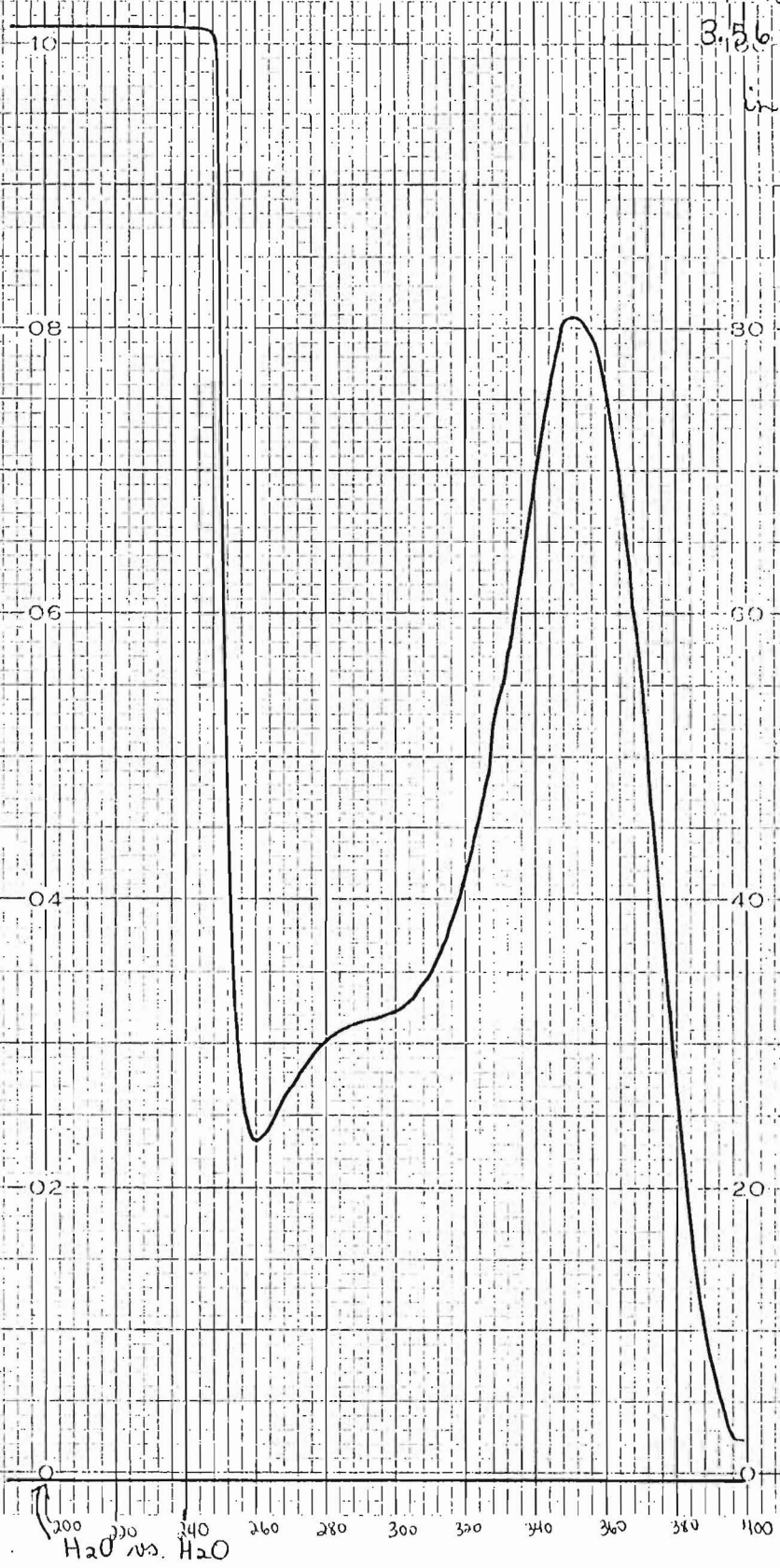
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S#1

9-18-92

 $3.56 \times 10^{-2} M$   
NaNO<sub>2</sub>  
in water400-190 nm  
120 nm/min  
chart 20 nm/cm  
slit = ~~0.25~~ nm  
1.0

0 - 1.00 A units

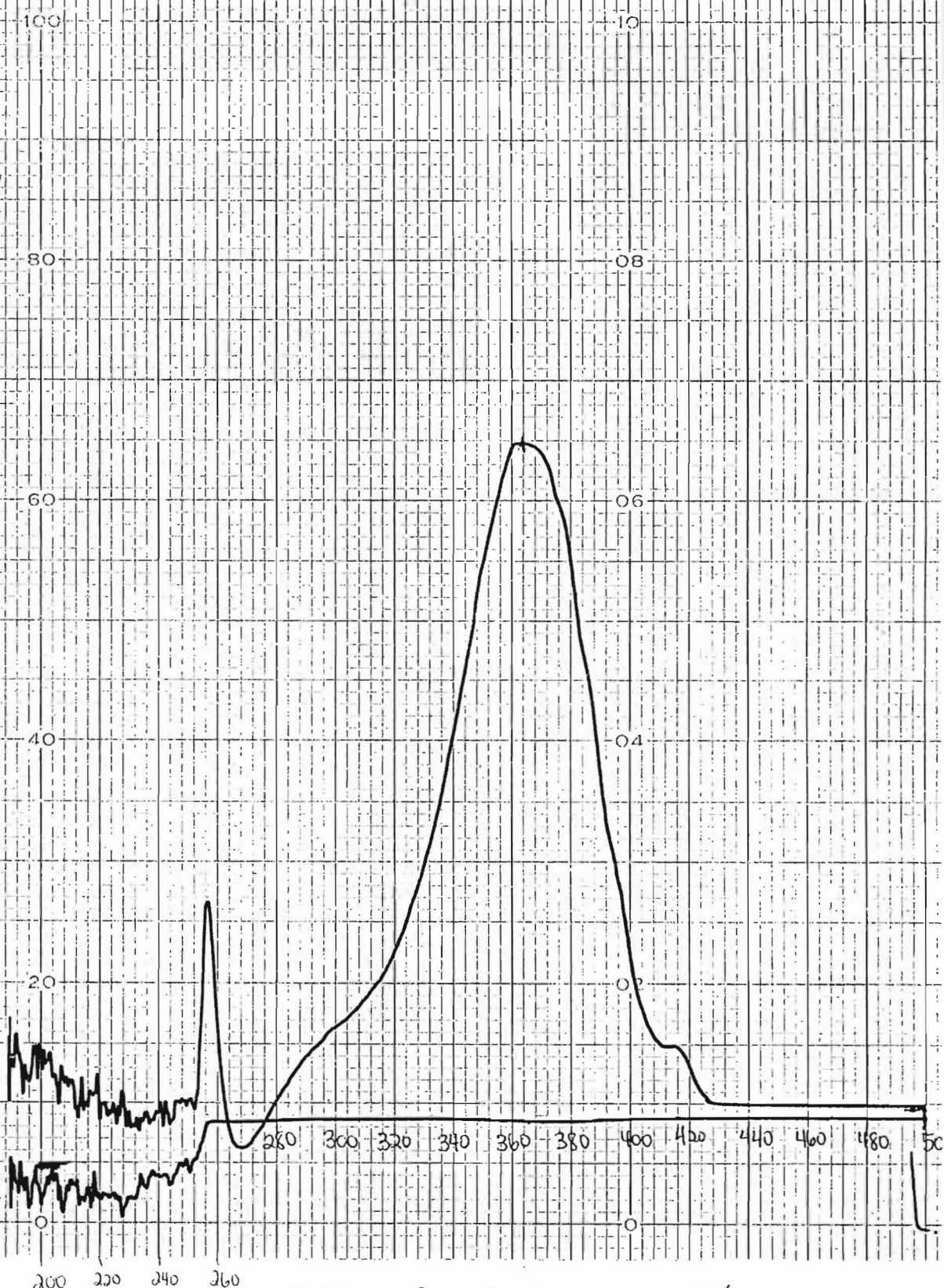
H<sub>2</sub>O vs. H<sub>2</sub>O



S#2 9-23-92

500-190 nm  
 10 nm/min  
 slit 20 nm/cm  
 slit = 0.25 nm

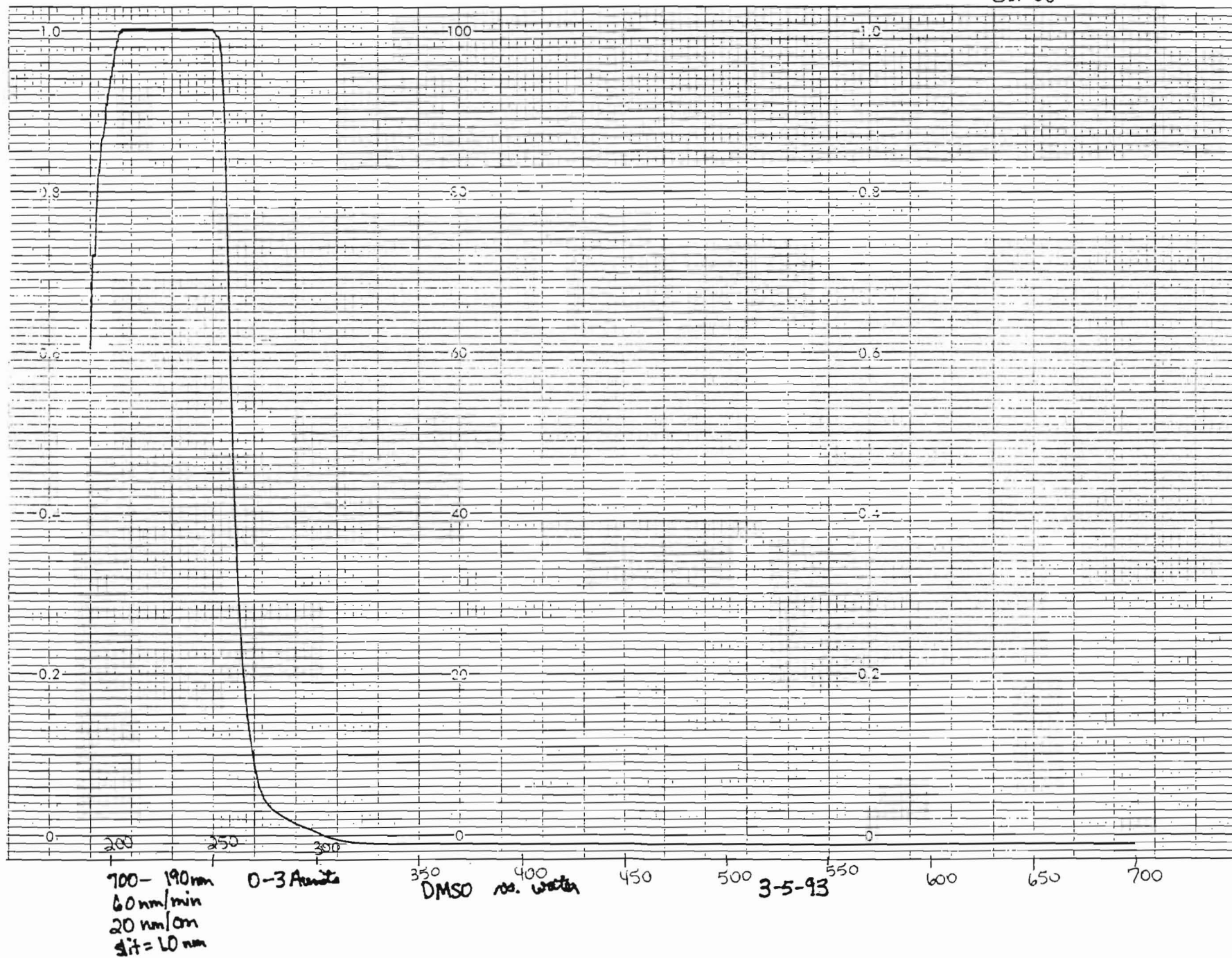
0.100 to 1.00 Absorbance



$3.41 \times 10^{-2} \text{ M NaNO}_2$   
 in DMSO  $\lambda_{\text{max}} \approx 365$

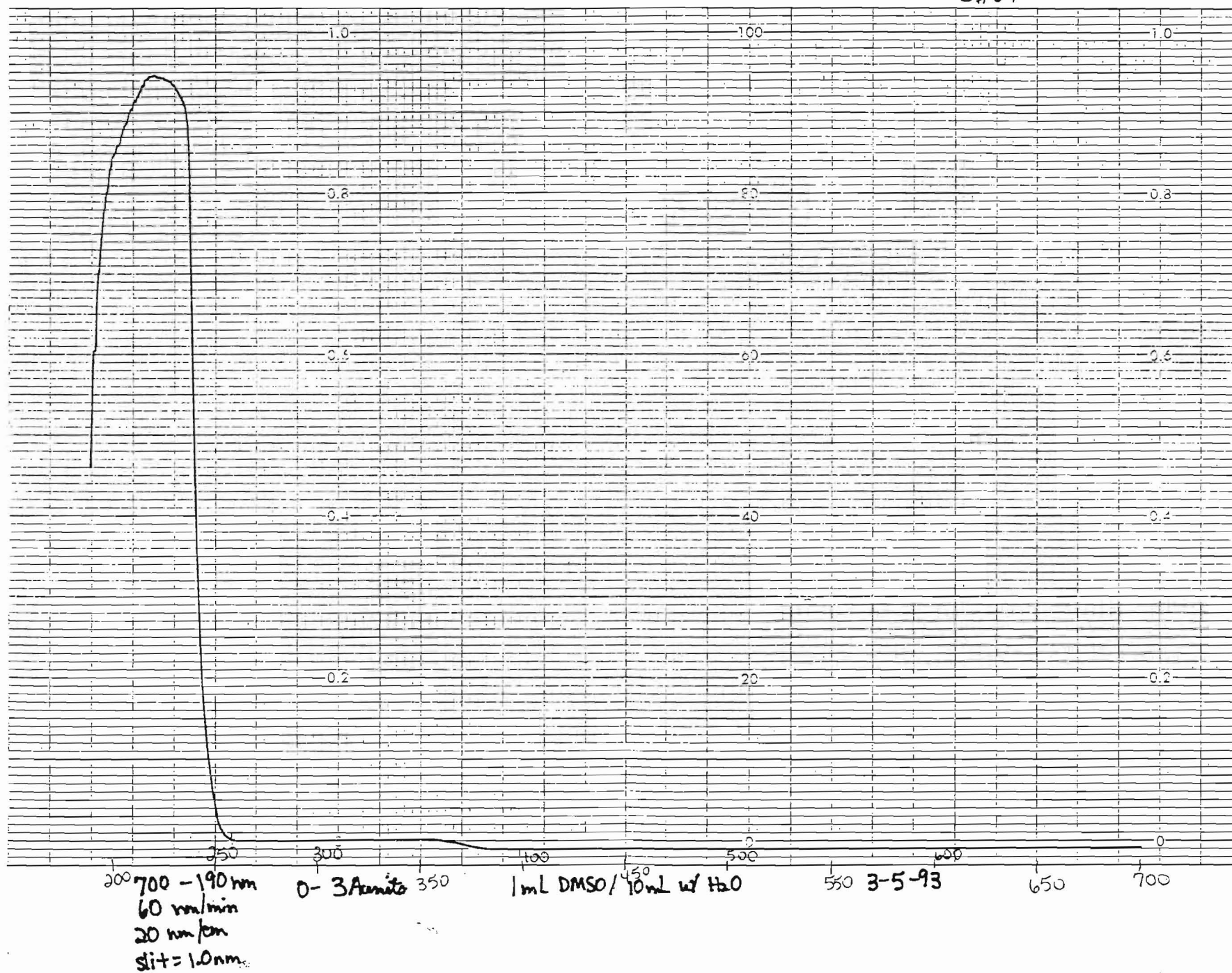


S# 66

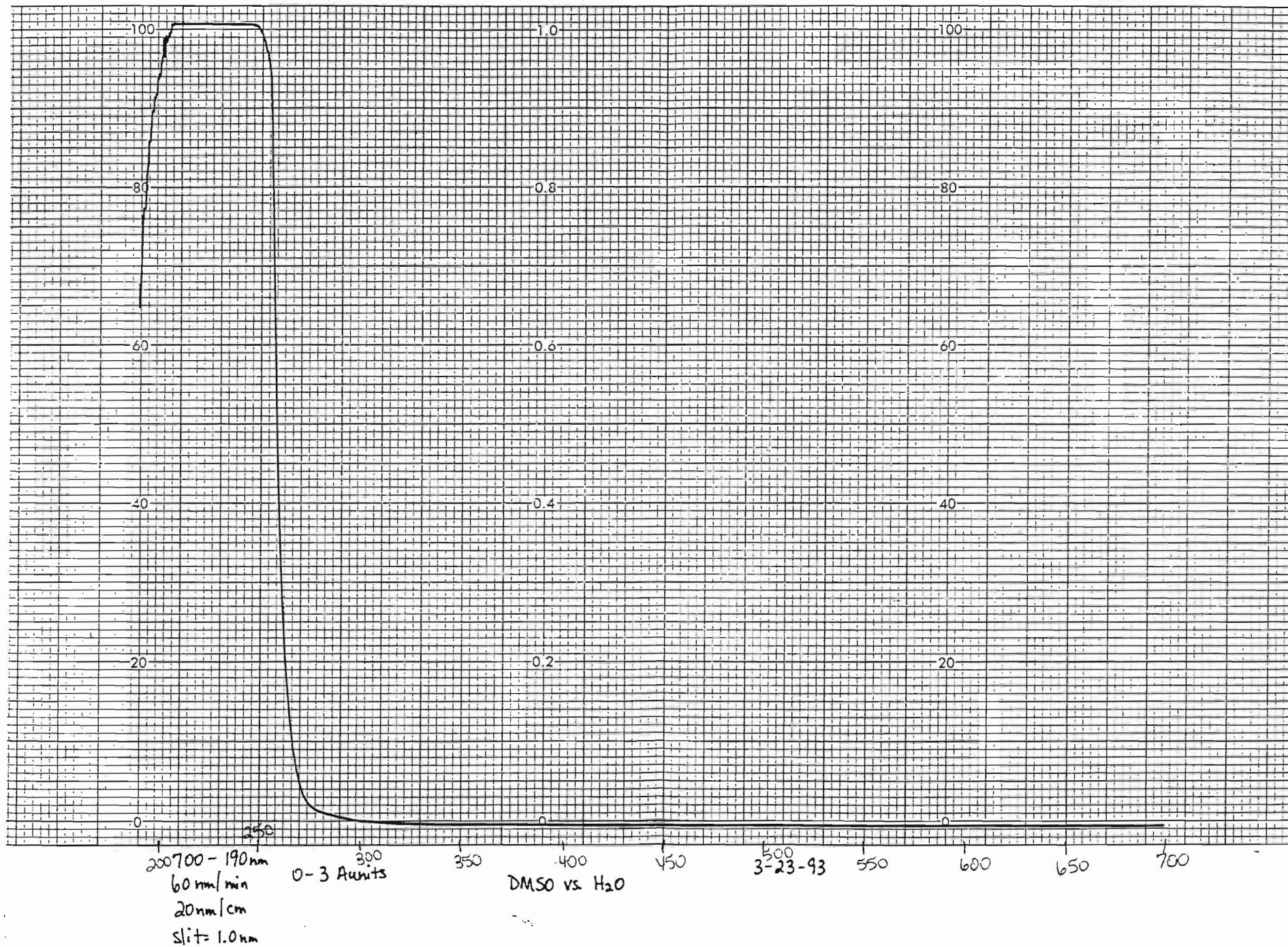


S#67

A 4



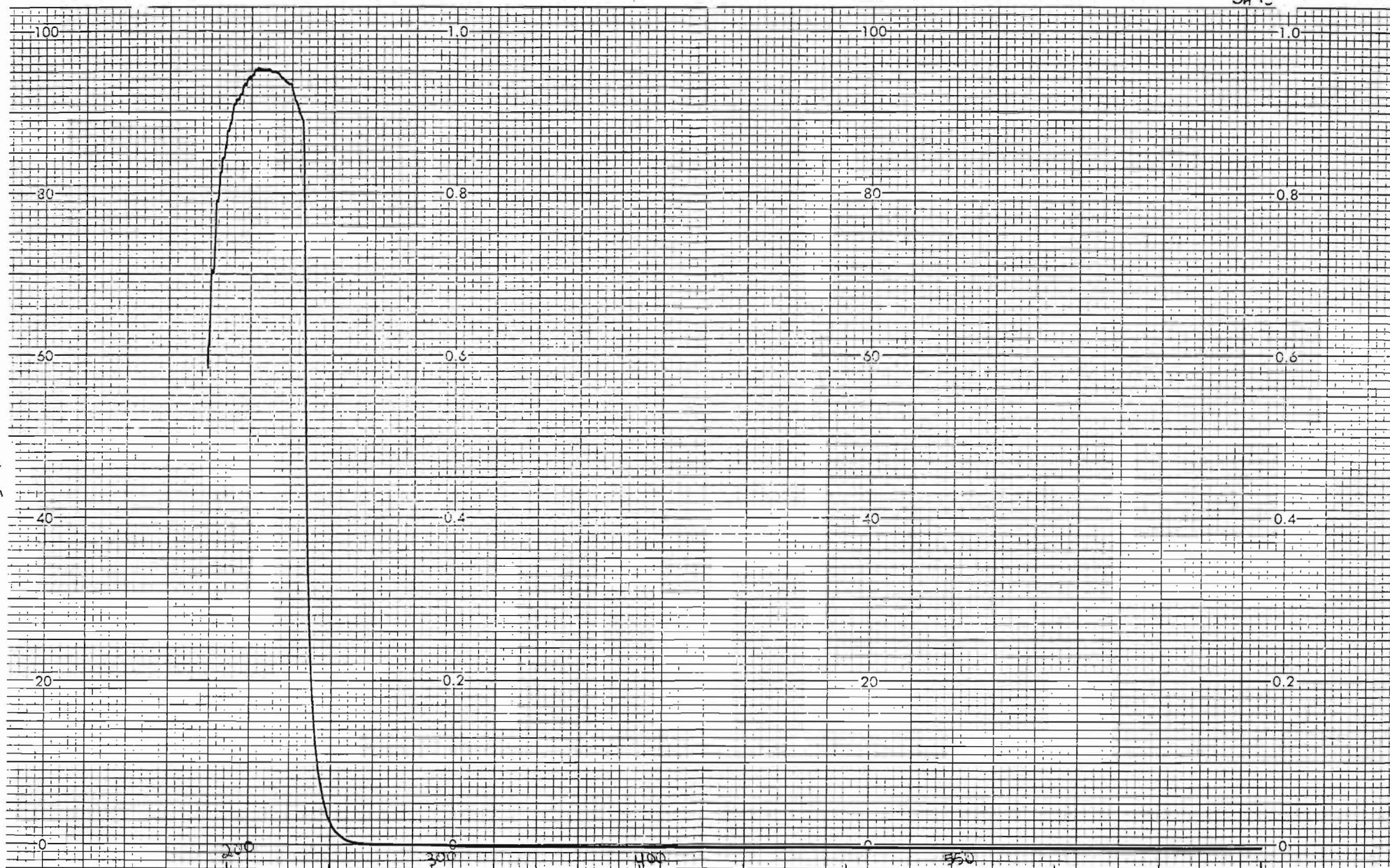
S# 72





SA71

A 6



700-190 nm  
60 nm/min  
20 nm/cm  
Slit=1.0 nm

250

0-3A units

350

1:10 dilution  
DMSO in H<sub>2</sub>O vs H<sub>2</sub>O

450

500

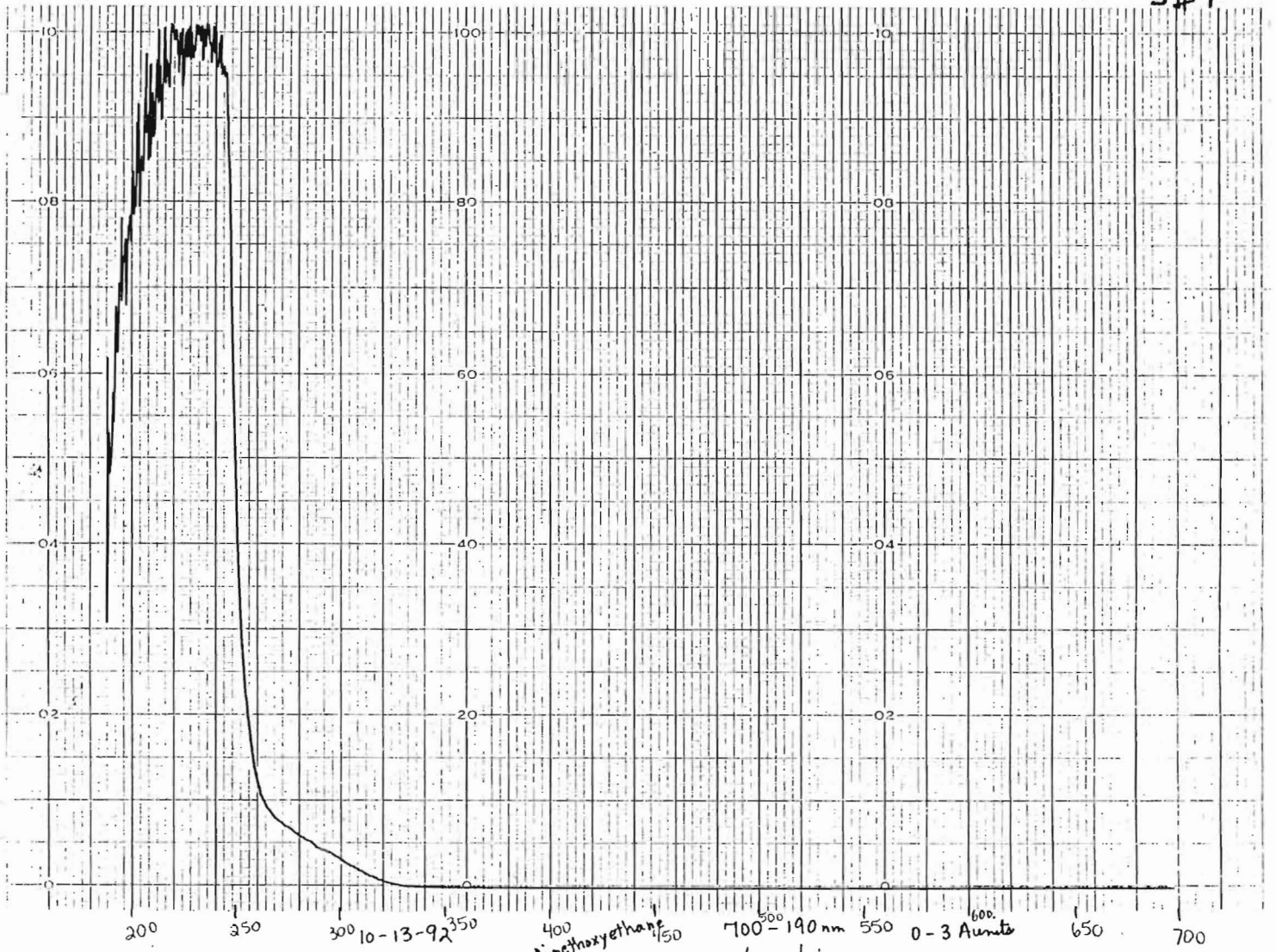
3-23-93

600

650

700

S#9

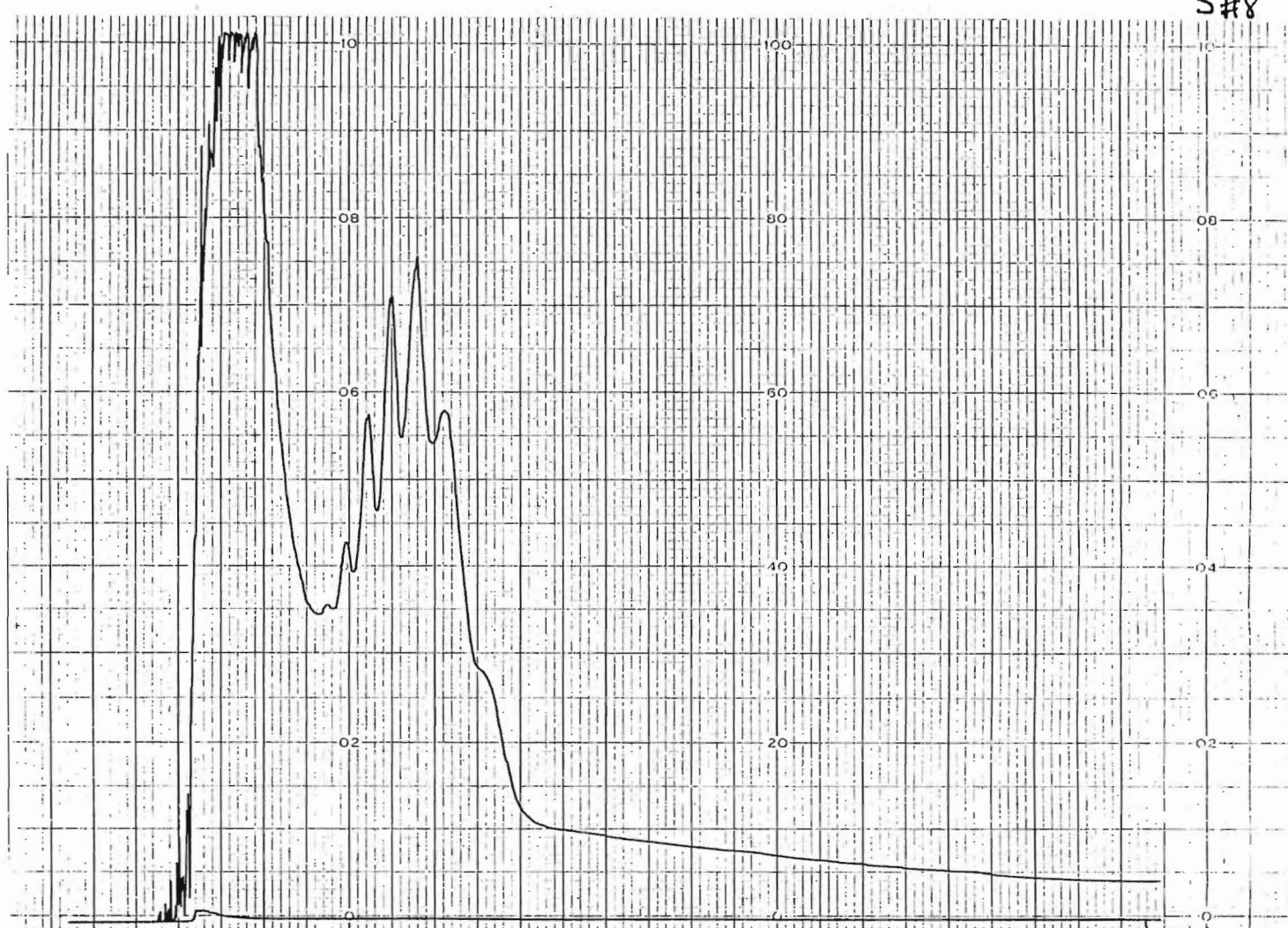


PART NO. B0093925

PERKIN ELMER

PART NO. B0093925

S#8



200 250 300 350 400 450 500 550 600 650 700

10-13-92  
700-190 nm  
60 nm/min  
20 cm/min

Slit = 1.0 nm  
0-3 Abs units

"saturated"  $\text{NaNO}_2$   
in 1,2-dimethoxyethane

Solvent vs. 70% solvent

PERKIN ELMER

PART NO. 80093925

PERKIN ELMER

PART



S#19



"saturated"  $\text{NaNO}_2$   
in "dry" 1,2-DME

500-190 nm  
60 nm/min  
20 cm/min  
Slit = 1.0 nm

11-6-92

0-3+  
0-1 A units

PART NO. B0093925

PERKIN ELMER

St# 20



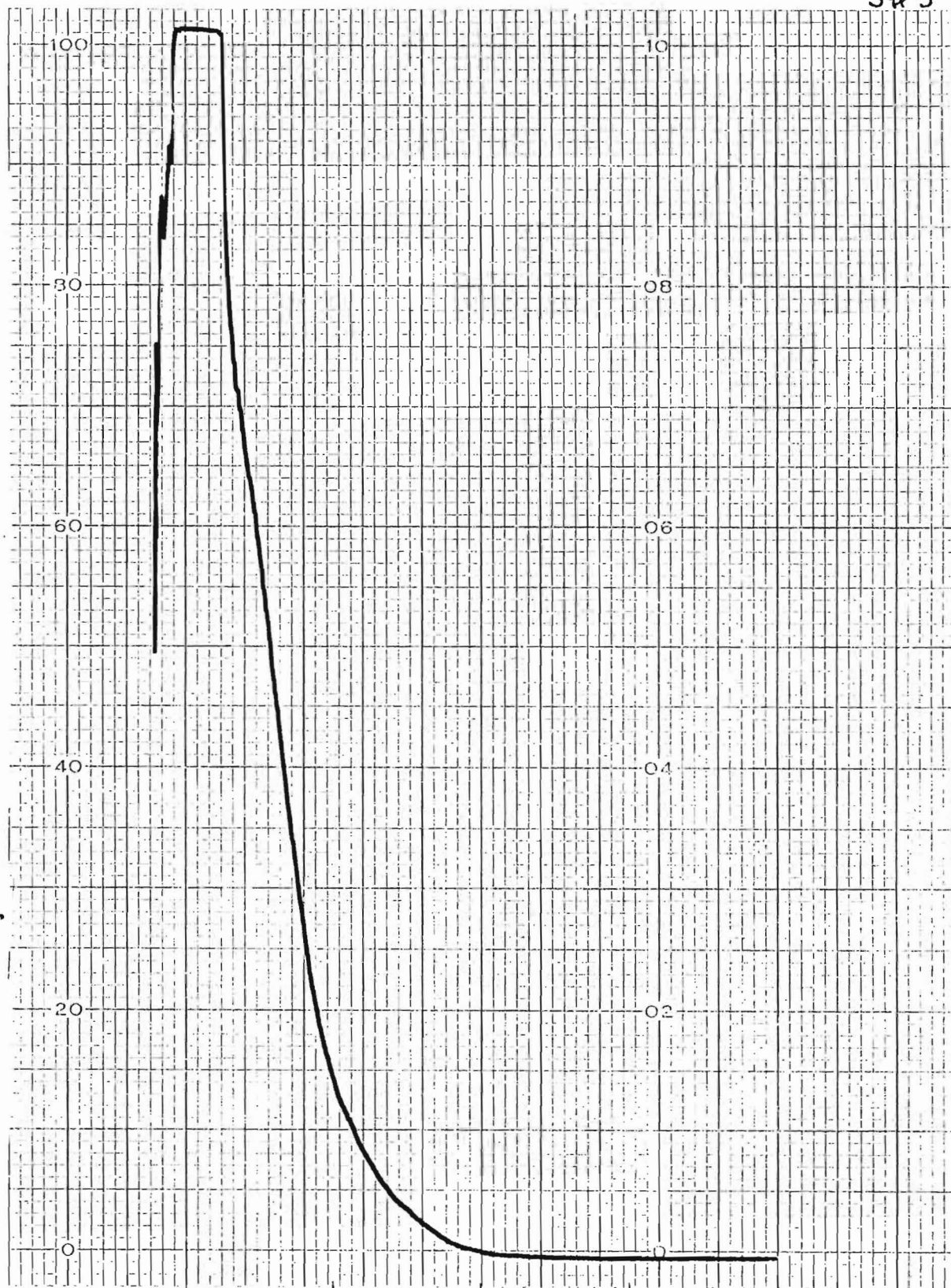
"saturated"  $\text{NaNO}_2$   
in "dry" 1,2-DME

500-190 nm  
60 nm/min  
20 cm/min  
Slit=1.0 nm

0-3 Aunits  
11-6-92



S# 3



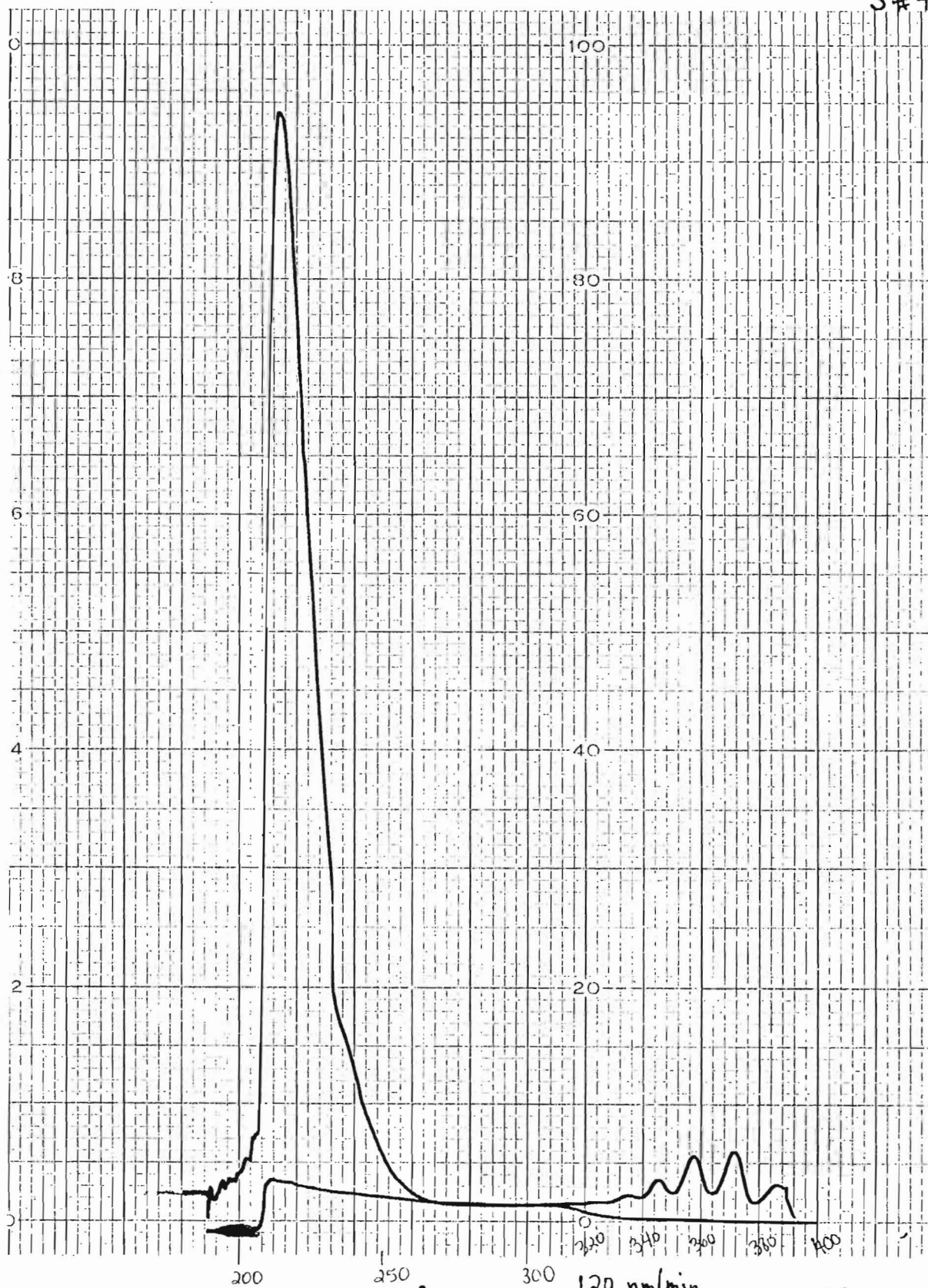
200 250 300 350 400  
 p-Dioxane vs. H<sub>2</sub>O  
 400 - 190 nm  
 0 - 2 Absorbers  
 60 nm/min  
 20 cm/min  
 slit = 1.0 nm  
 9-30-92

PERKIN ELMER

PART NO. B009392

☐ ☐ ☐ A11 ☐ ☐ ☐

S#4



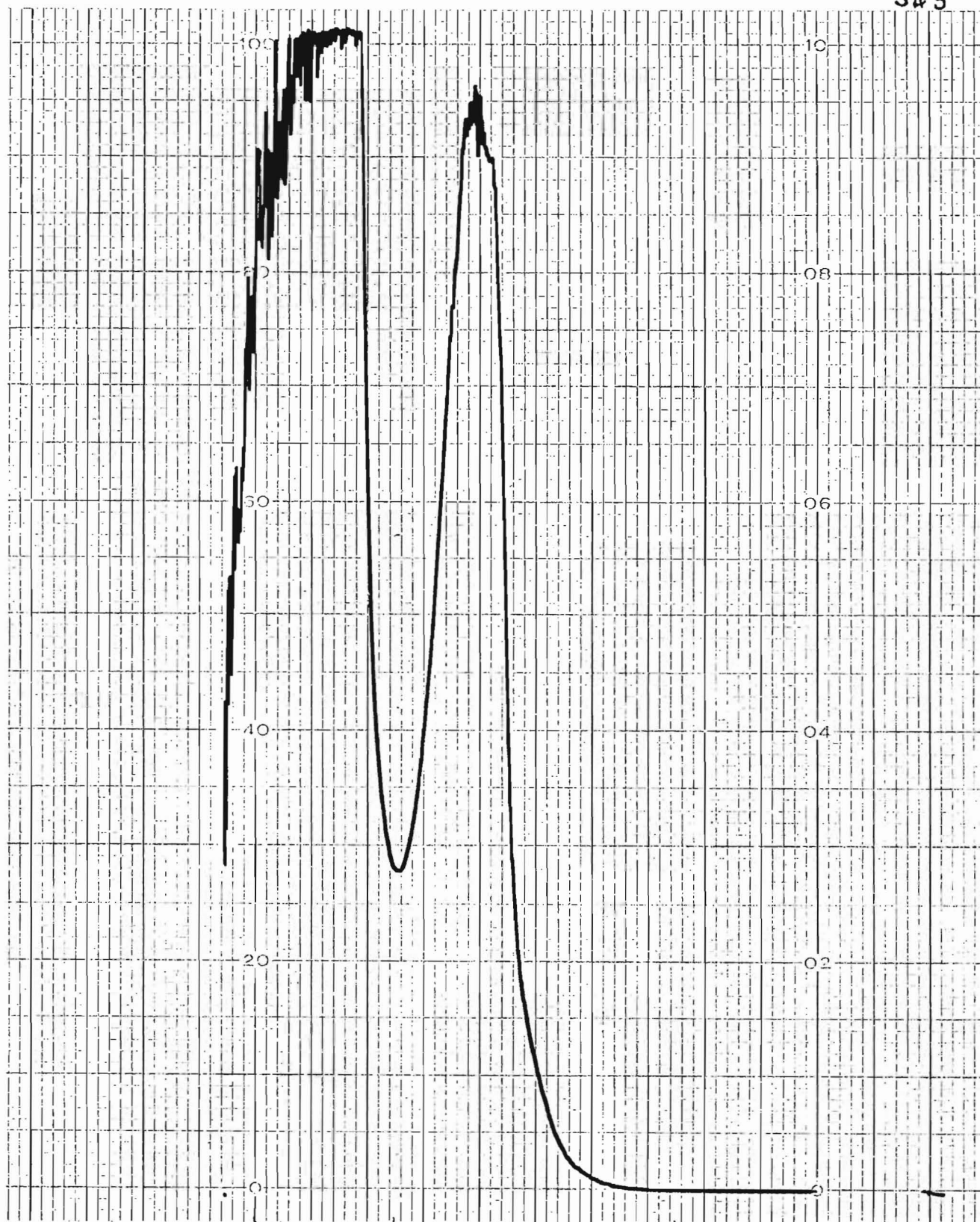
"saturated"  
NaNO<sub>2</sub>  
in P-Dioxane

120 nm/min  
20 nm/cm  
slit 0.25 nm  
0 - 1.0 A units  
400 - 190 nm  
9-30-92  
PERKIN ELMER

PART NO. B0093925

A12

S# 5



400 - 190 nm  
60 nm/min  
20 cm/min  
slit = 1.0 nm  
0 - 3 A units

THF vs. H<sub>2</sub>O

9-30-92

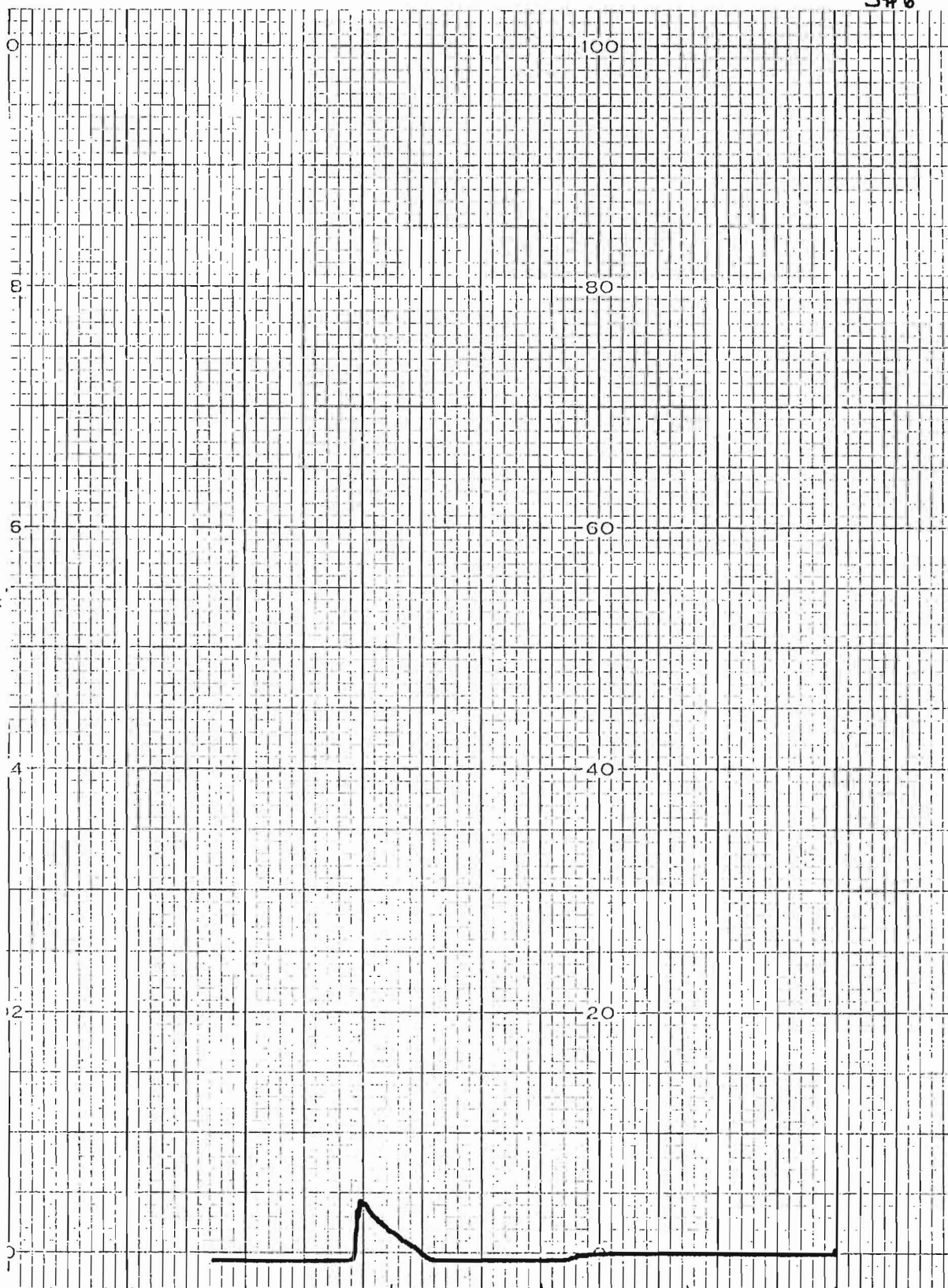
PERKIN-ELMER

PART NO. 1

A13



S#6

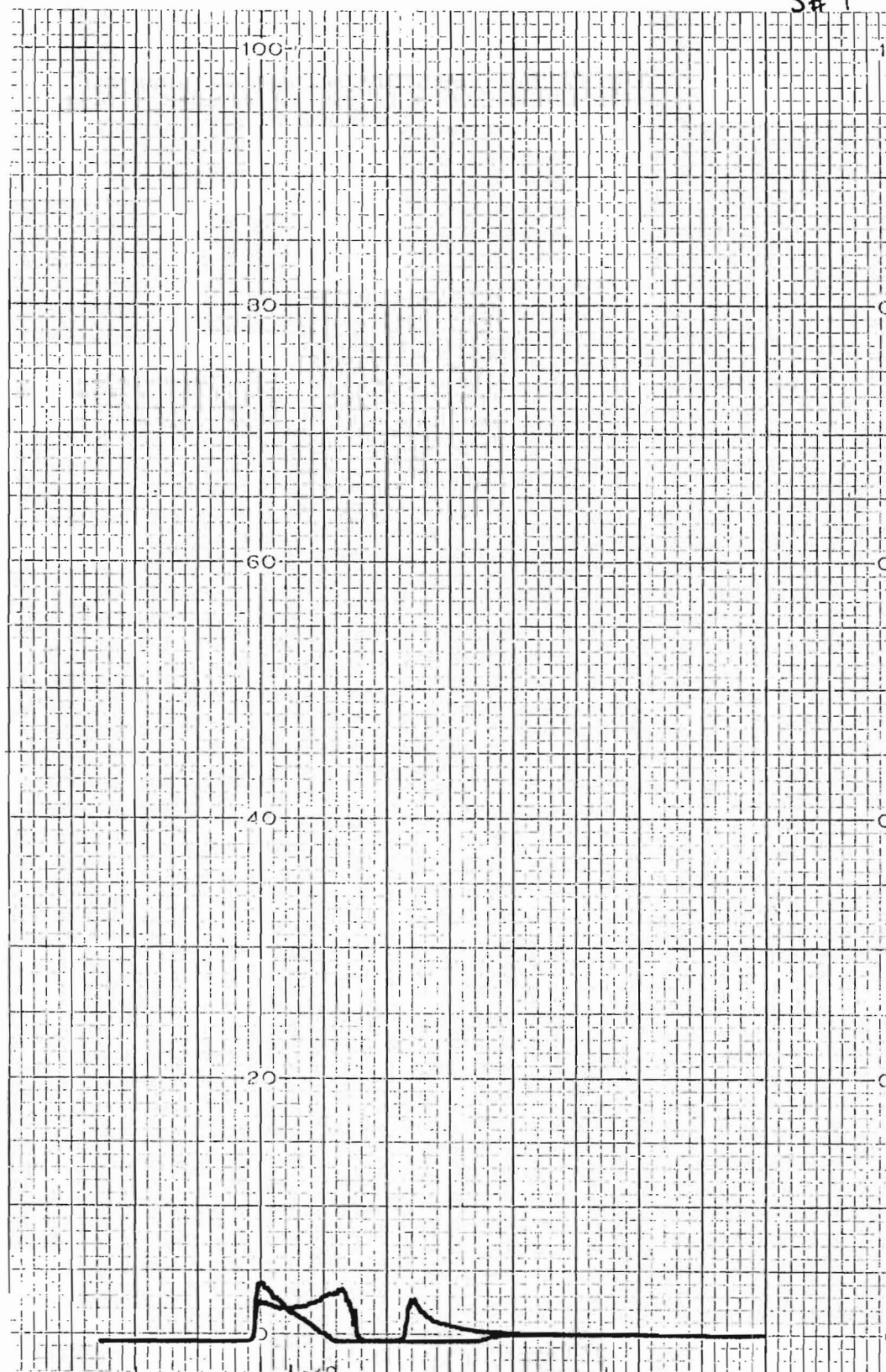


NaNO<sub>2</sub> "saturated"  
THF

400-190nm  
60nm/min  
20 cm/min  
0-2 Abs units  
slit = 1.0nm

9-30-92

S#7



200 250 300 350 400  
THF no. THF  
NaNO<sub>2</sub> "saturated"  
THF  
400-190 nm  
60 nm/min  
20 cm/min  
0-2 Aunits  
Slit = 1.0 nm  
9-30-92

PERKIN ELMER

☐ ☐ ☐ A15 ☐ ☐ ☐

S#11



10-14-92

400 - 190 nm  
60 nm/min  
20 cm/min  
0-3 A units  
Slit = 1.0 nm

acetonitrile  
vs  
H<sub>2</sub>O

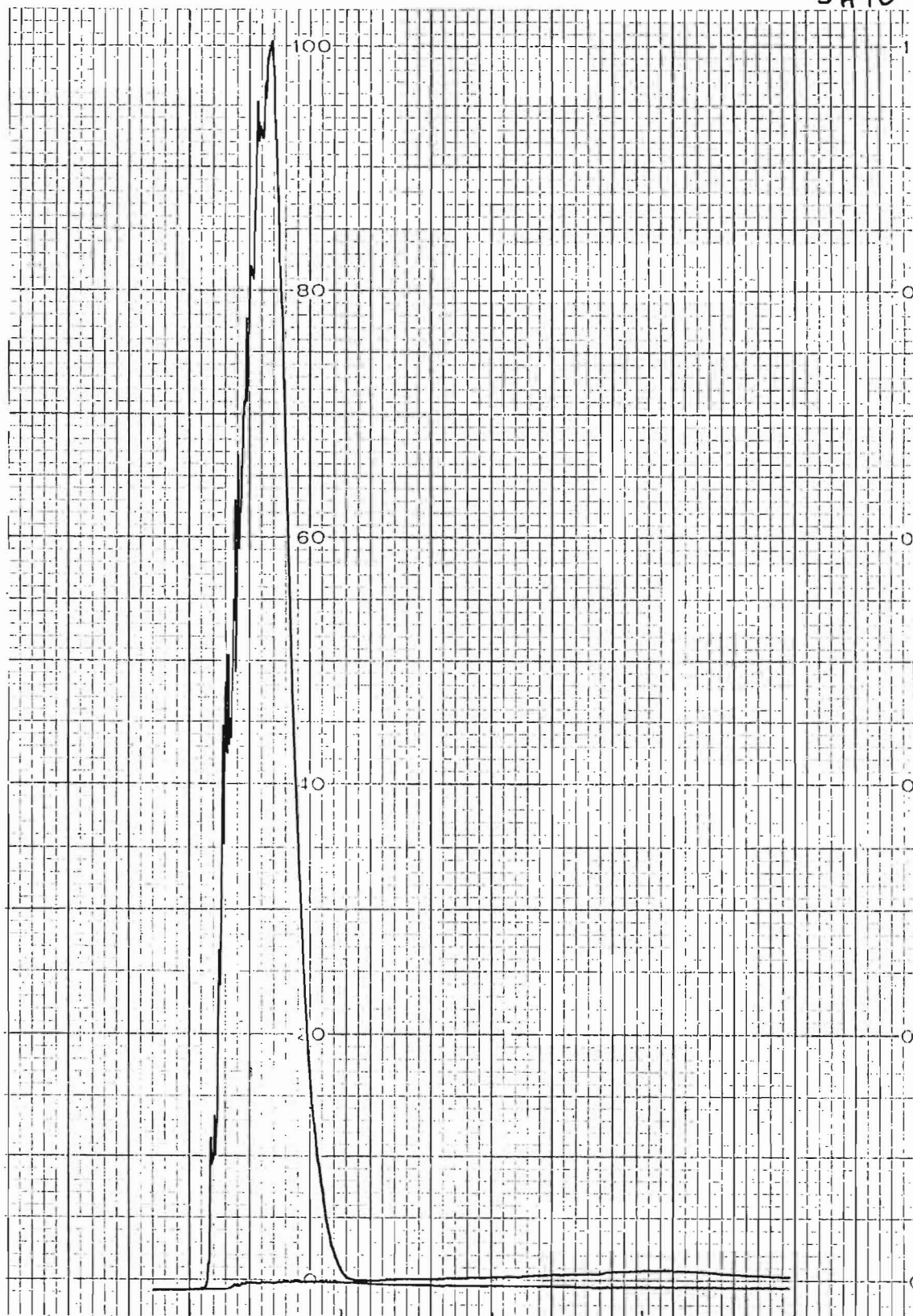
ELKIN ELMER

PART NO. B0093925

A16



S#10



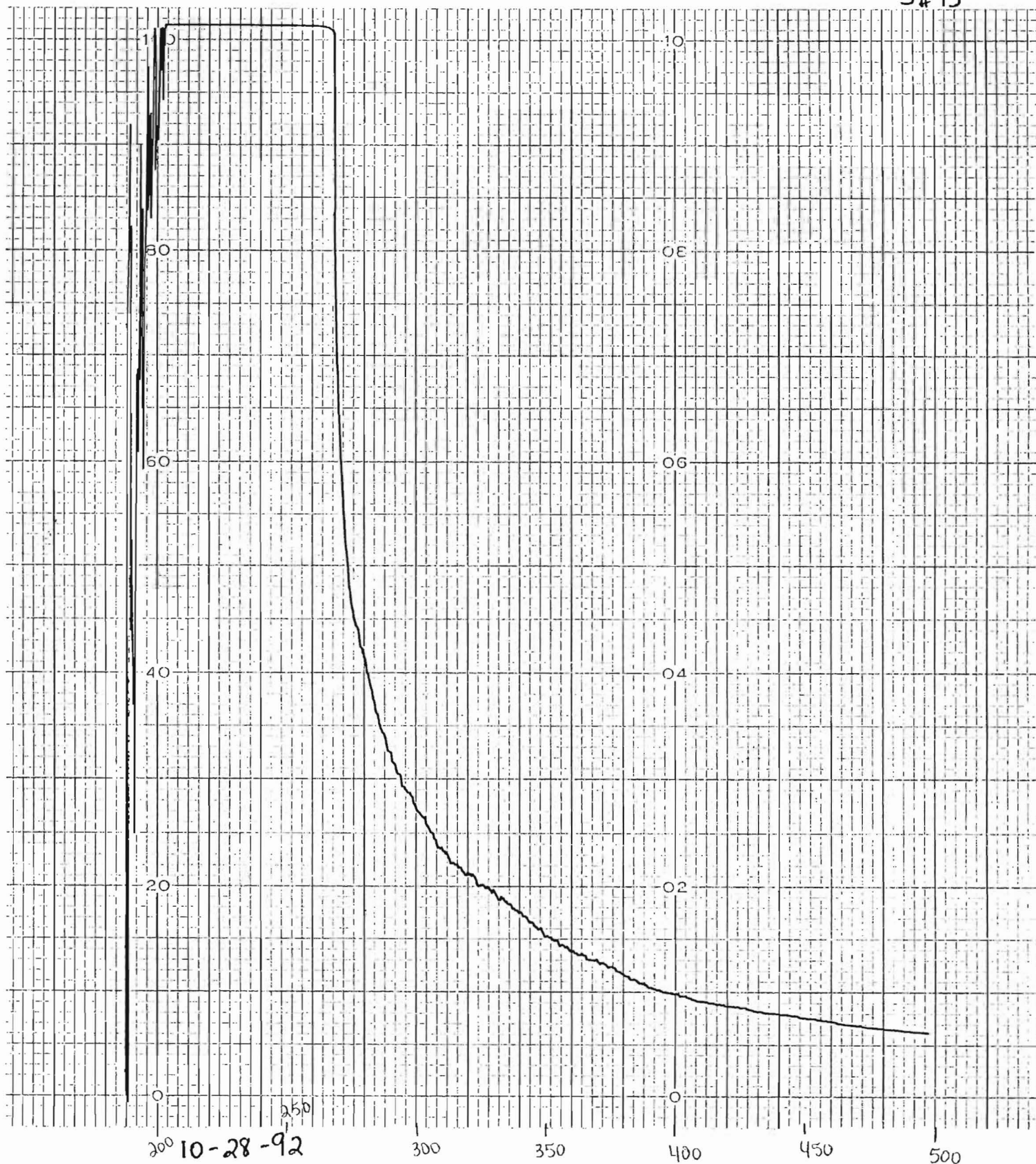
200 250  
10-14-92

400 - 190 nm  
60 nm/min  
20 cm/min  
0-2 A units

slit = 1.0 mm PERKIN-ELMER

300 350 400  
"Saturated"  
NaNO<sub>2</sub>  
in  
acetonitrile

S# 15



DMF vs. H<sub>2</sub>O

500 - 190 nm

60 nm/min

PERKIN ELMER

20 cm/min

Slit = 1.0 nm

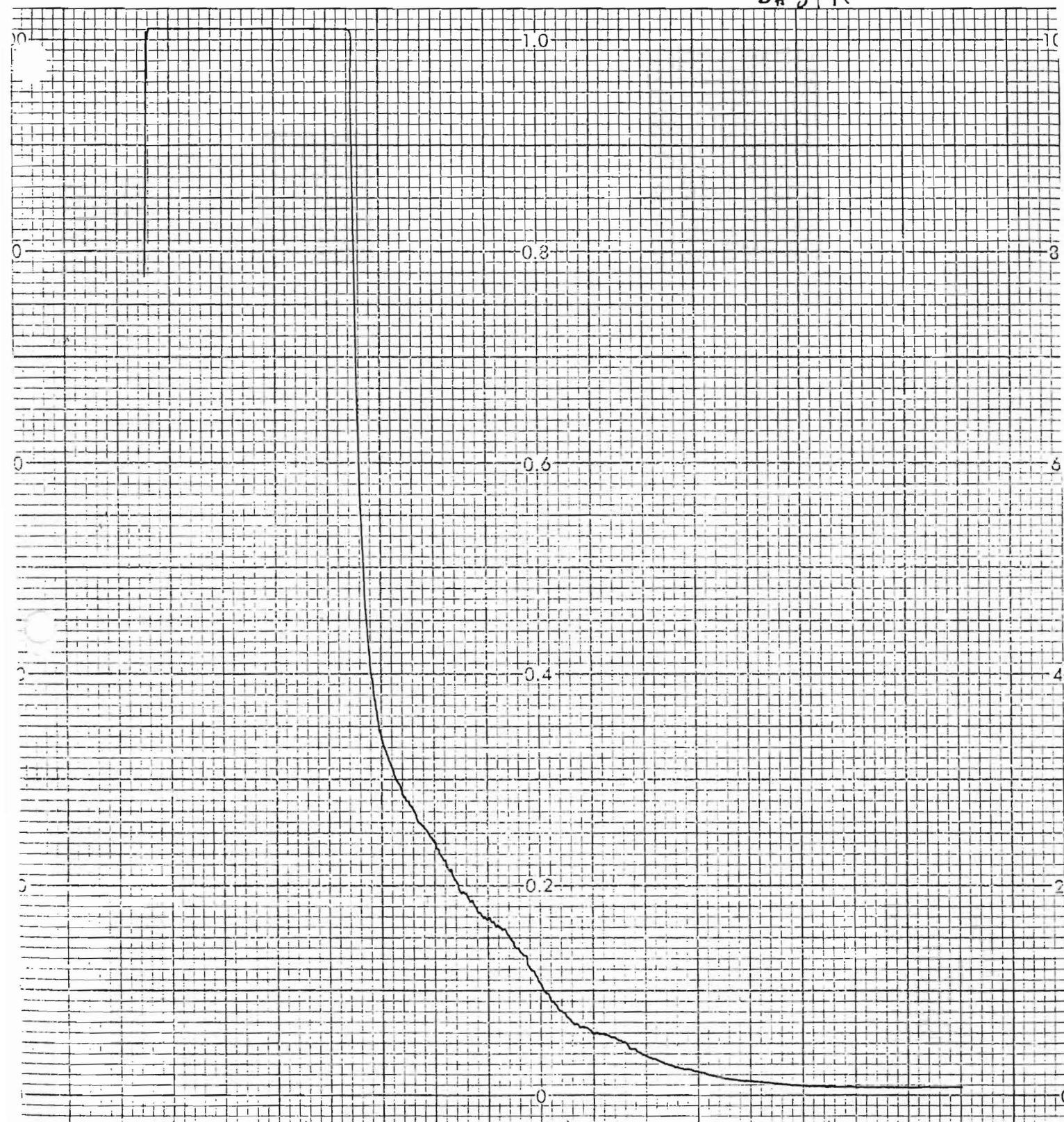
0 - 1 A unit

PART NO. B0093025

A18



S# 37 A



200 500 - 190 nm

60 nm/min

20 cm/min

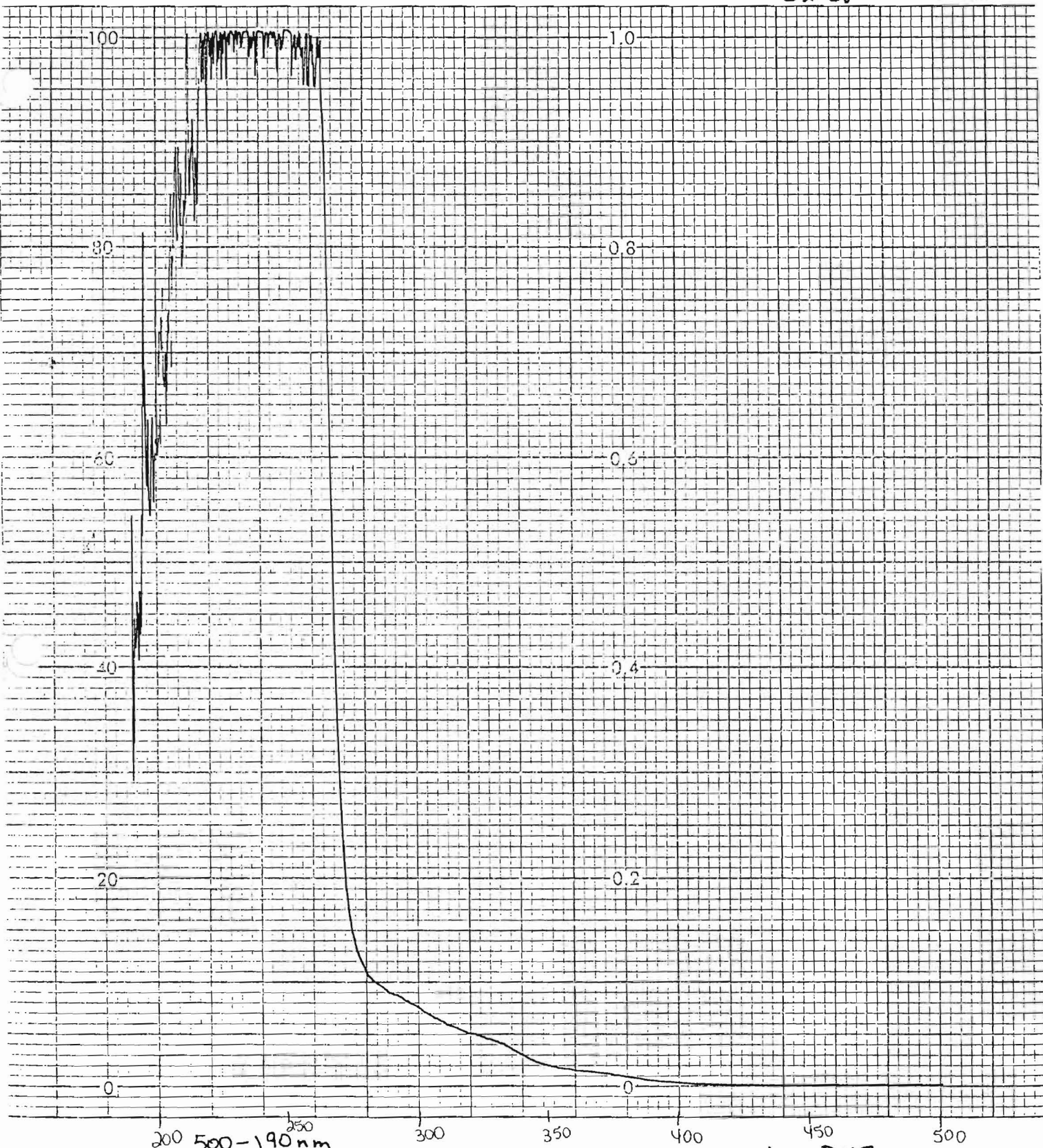
slit = 1.0 nm

0 - 1 A unit

11-20-92

dry DMF  
no. H<sub>2</sub>O

S# 38

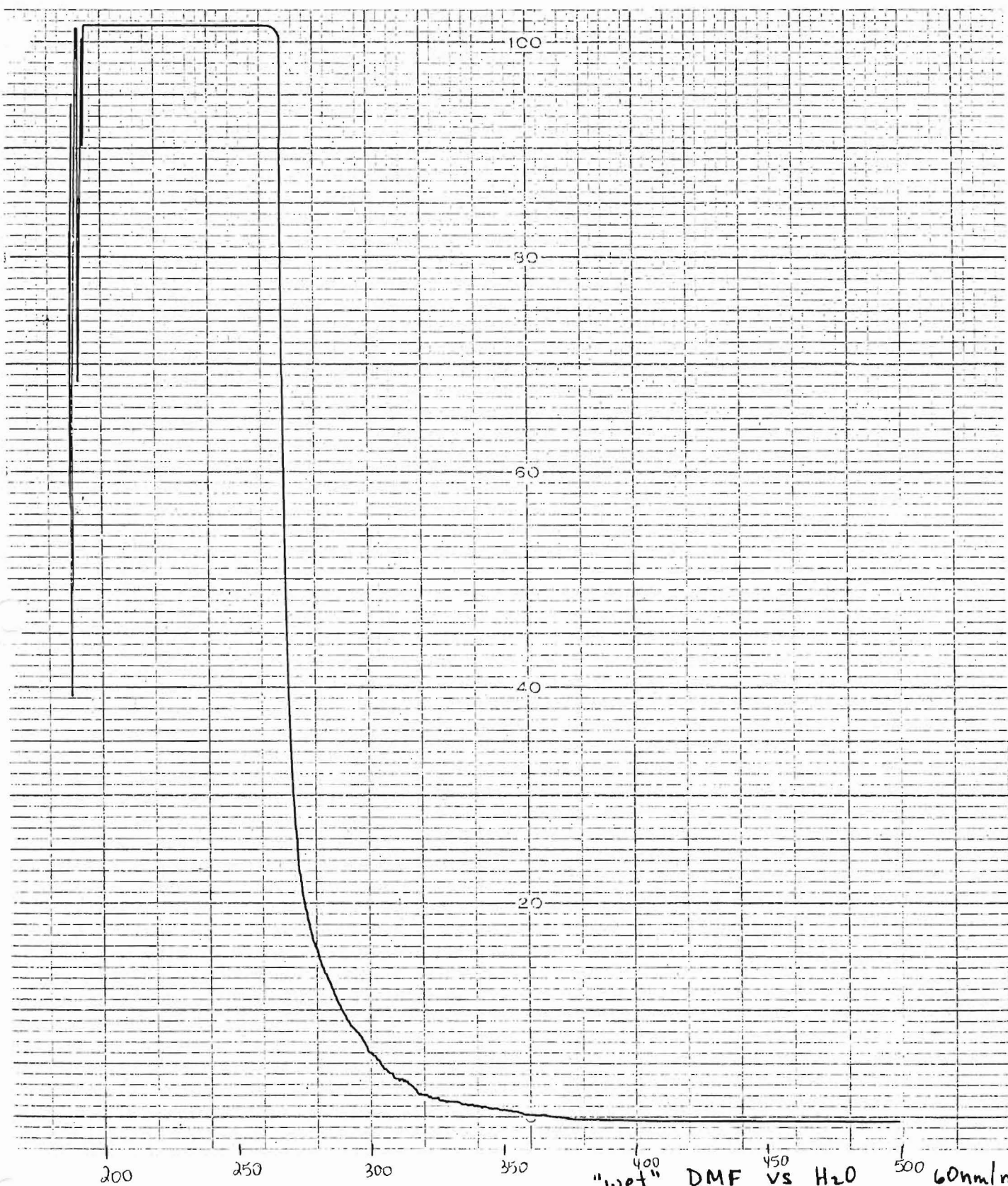


200 500-190 nm  
60 nm/min  
20 cm/min  
slit=1.0nm

0-3 Aunit

11-20-92

dry DMF  
vs. H<sub>2</sub>O



S#21

"wet" DMF vs H<sub>2</sub>O

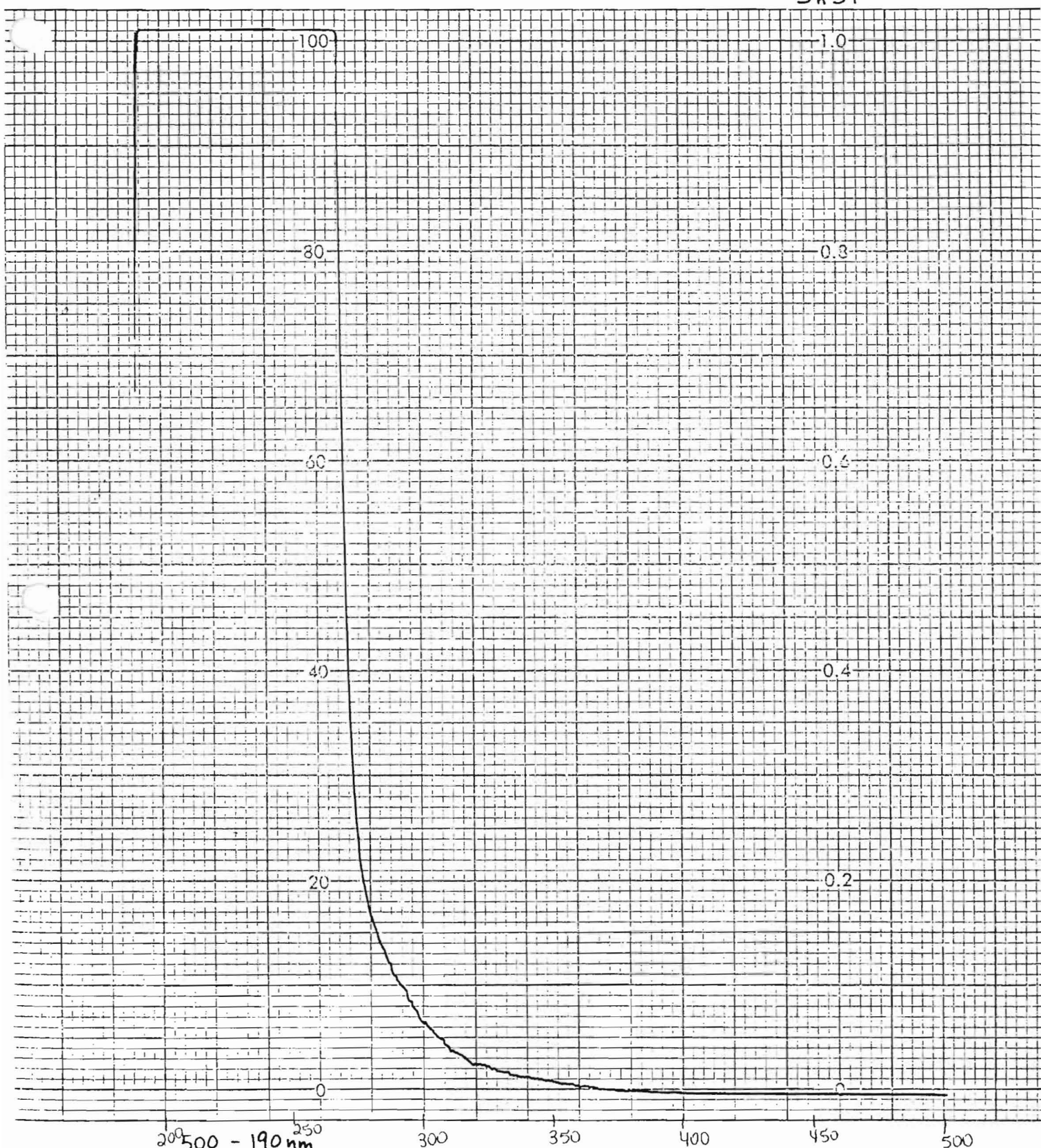
500-190nm

0-3 Aunit

60nm/min  
20 nm/cm  
slit = 1.0nm



S#39



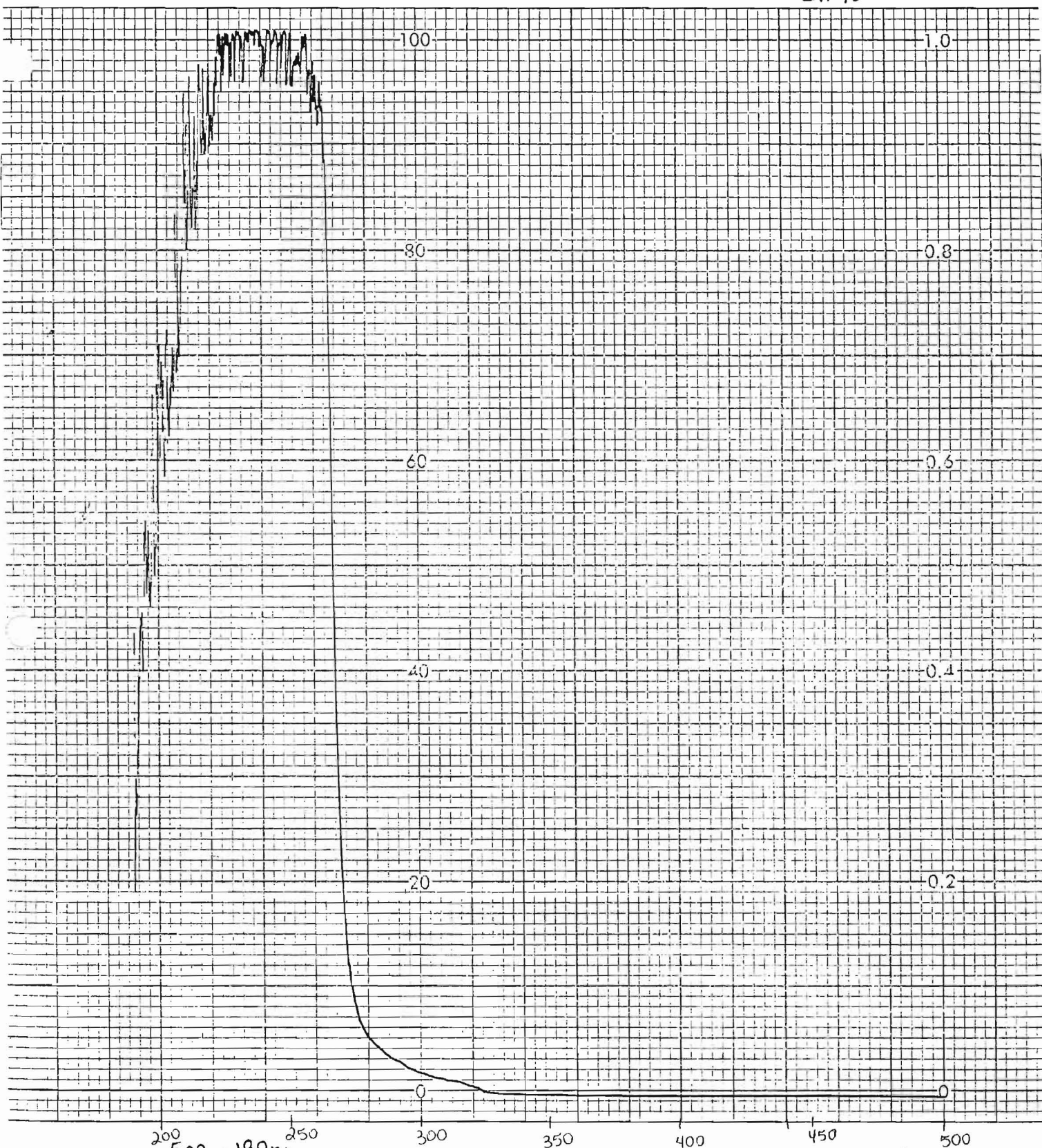
500 - 190 nm  
60 nm/min  
20 cm/min  
slit = 1.0 nm

0 - 1 A unit

11-20-92

wet DMF  
vs. H<sub>2</sub>O

S#40



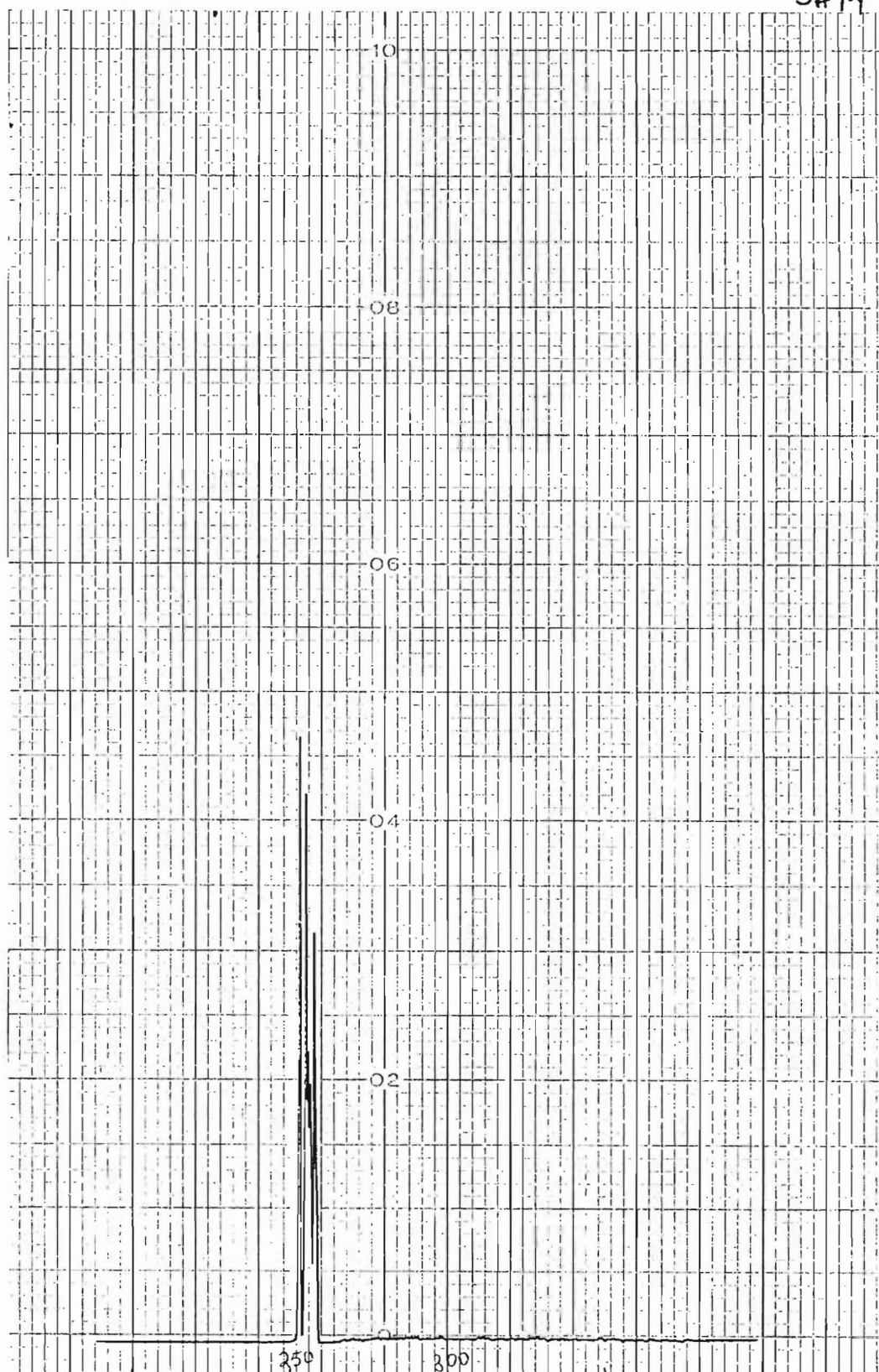
500 - 190 nm  
60 nm/min  
20 cm/min  
Slit = 1.0 nm

0-3 A unit

11-20-92

wet DMF  
vs. H<sub>2</sub>O

S#14



200 DMF solvent vs. solvent 350 400

10-28-92

400 - 190 nm  
120 nm/min  
20 cm/min  
slit = 1.0 nm

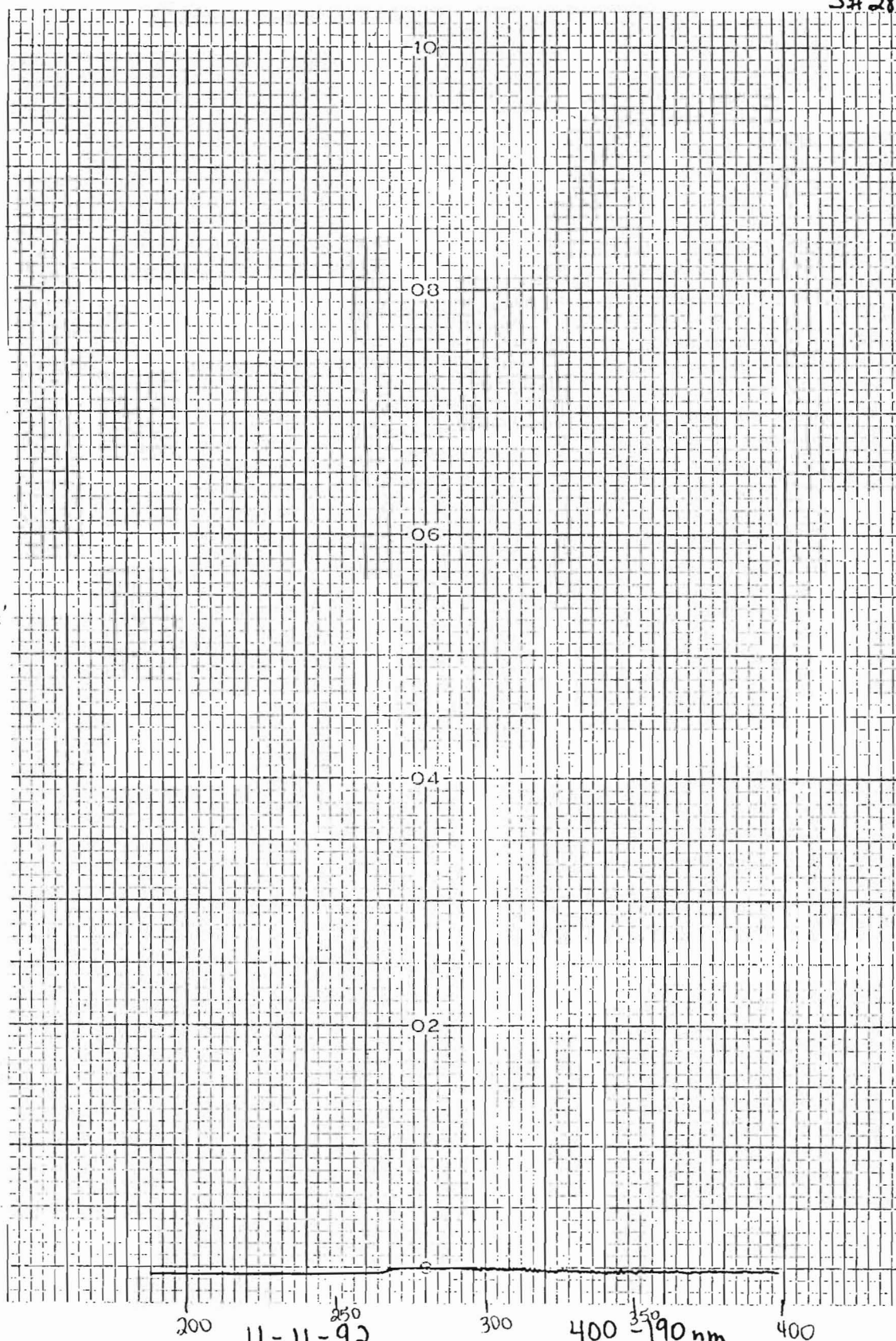
0 - 1 A unit

PART NO. B0093925

A24



S#28



11-11-92

400 350 nm

60 nm/min

20 cm/min

slit = 1.0 nm

0 - 1 A unit

MER

PART NO. B0093925

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A25

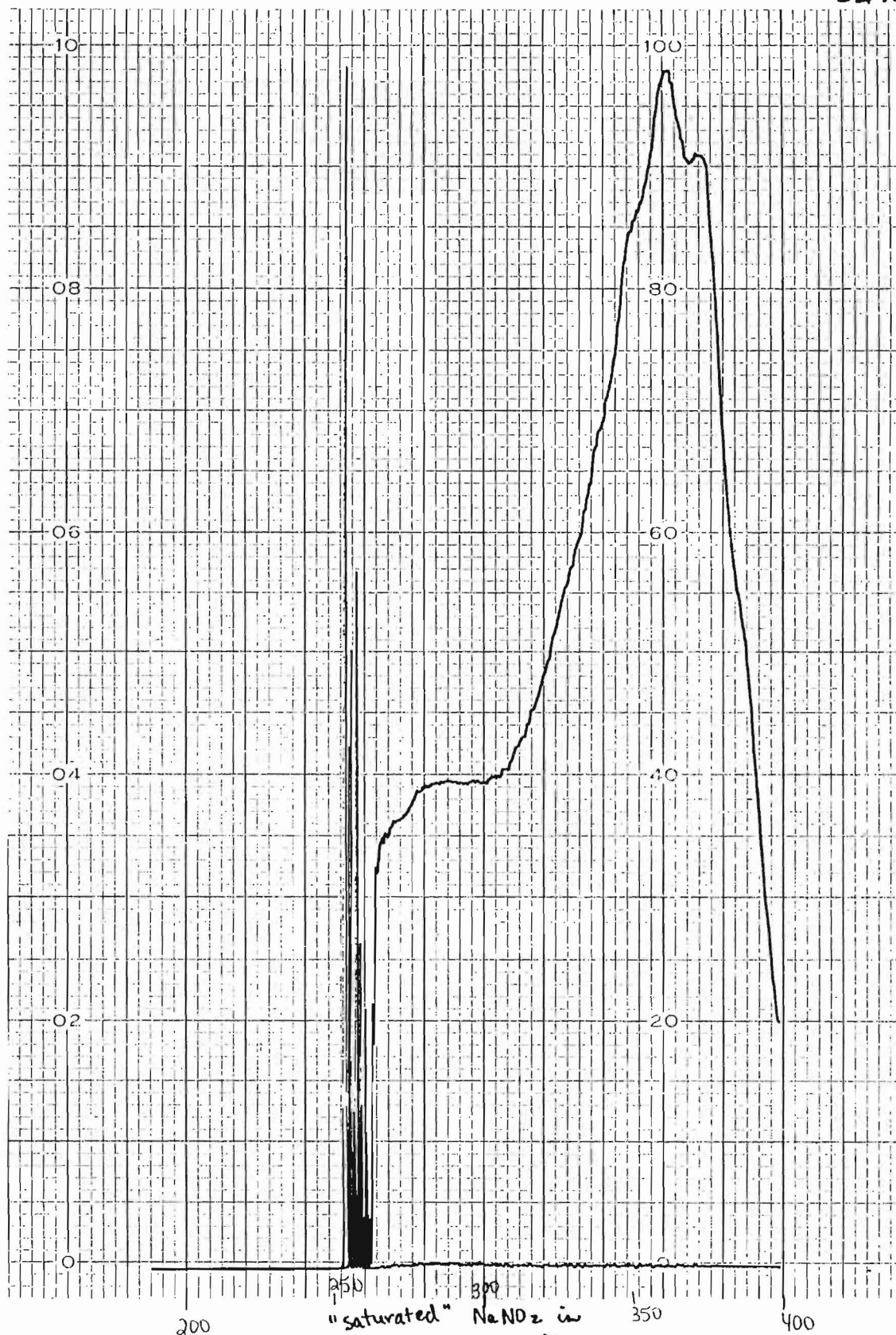
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S#12



250

300

350

400

"saturated"  $\text{NaNO}_2$  in  
DMF

400-190 nm

60 nm/min

20 cm/min

Slit = 1.0 nm

0-1 A unit

10-28-92

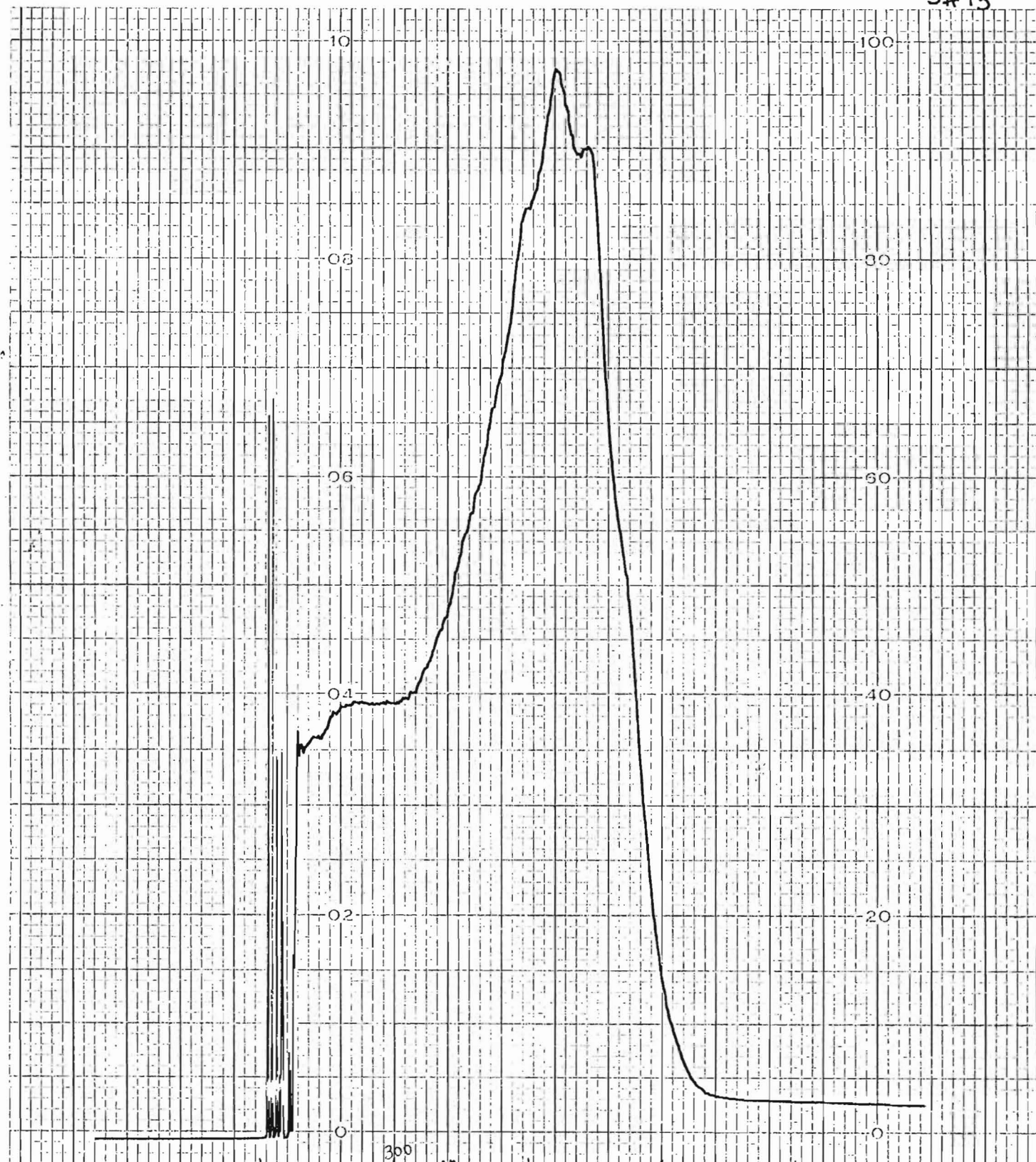
PART NO. B0093925

PERKIN ELMER

A26



S# 13



"saturated"  
NaNO<sub>2</sub> in  
DMF

500 - 190 nm  
60 nm/min  
20 cm/min  
slit = 1.0 nm  
0 - 1 Aunits

10-28-92

0-1 Abs +

Slit 1.0 nm

20 cm/min

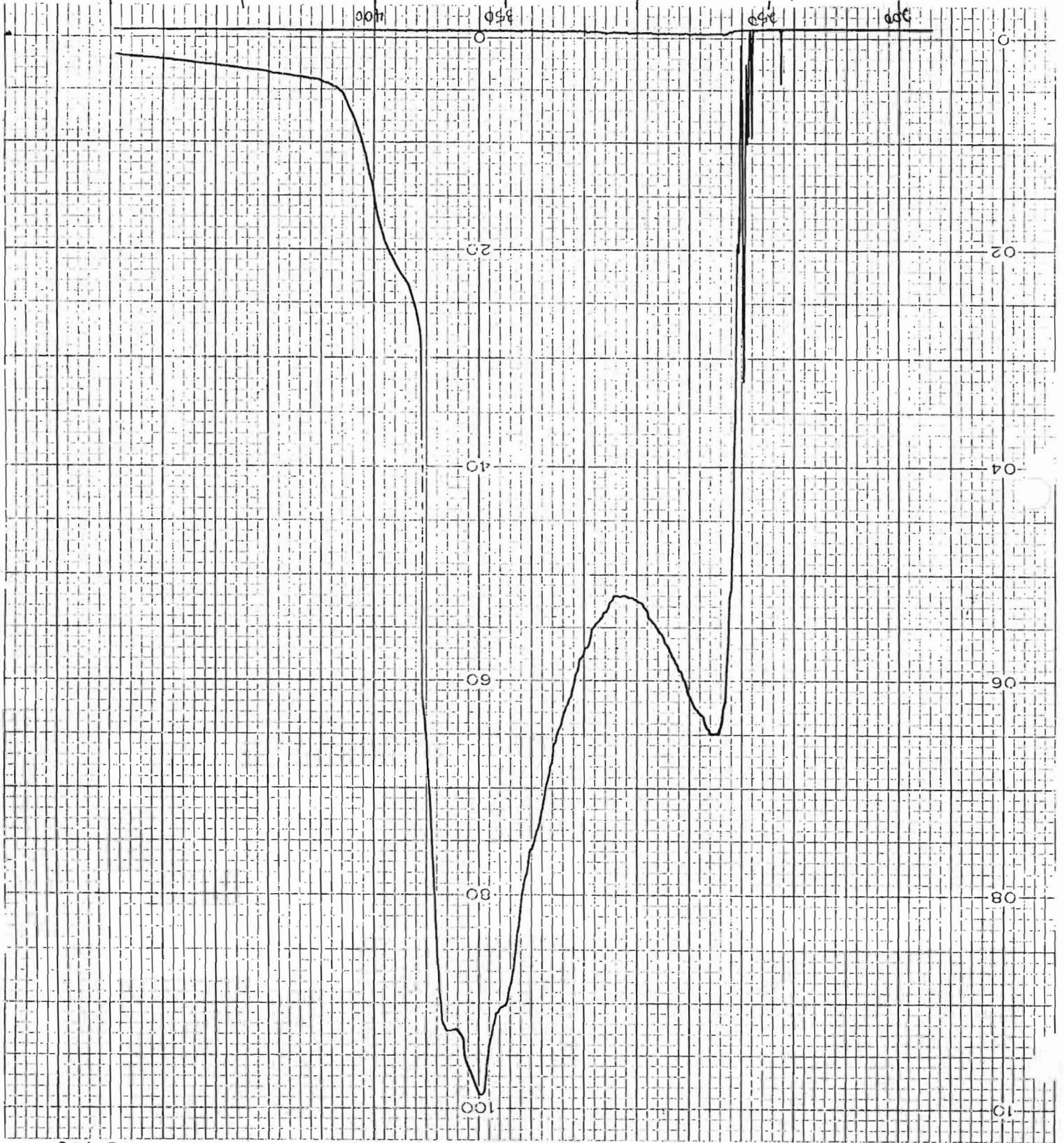
60 nm/min

500-190 nm

11-4-92

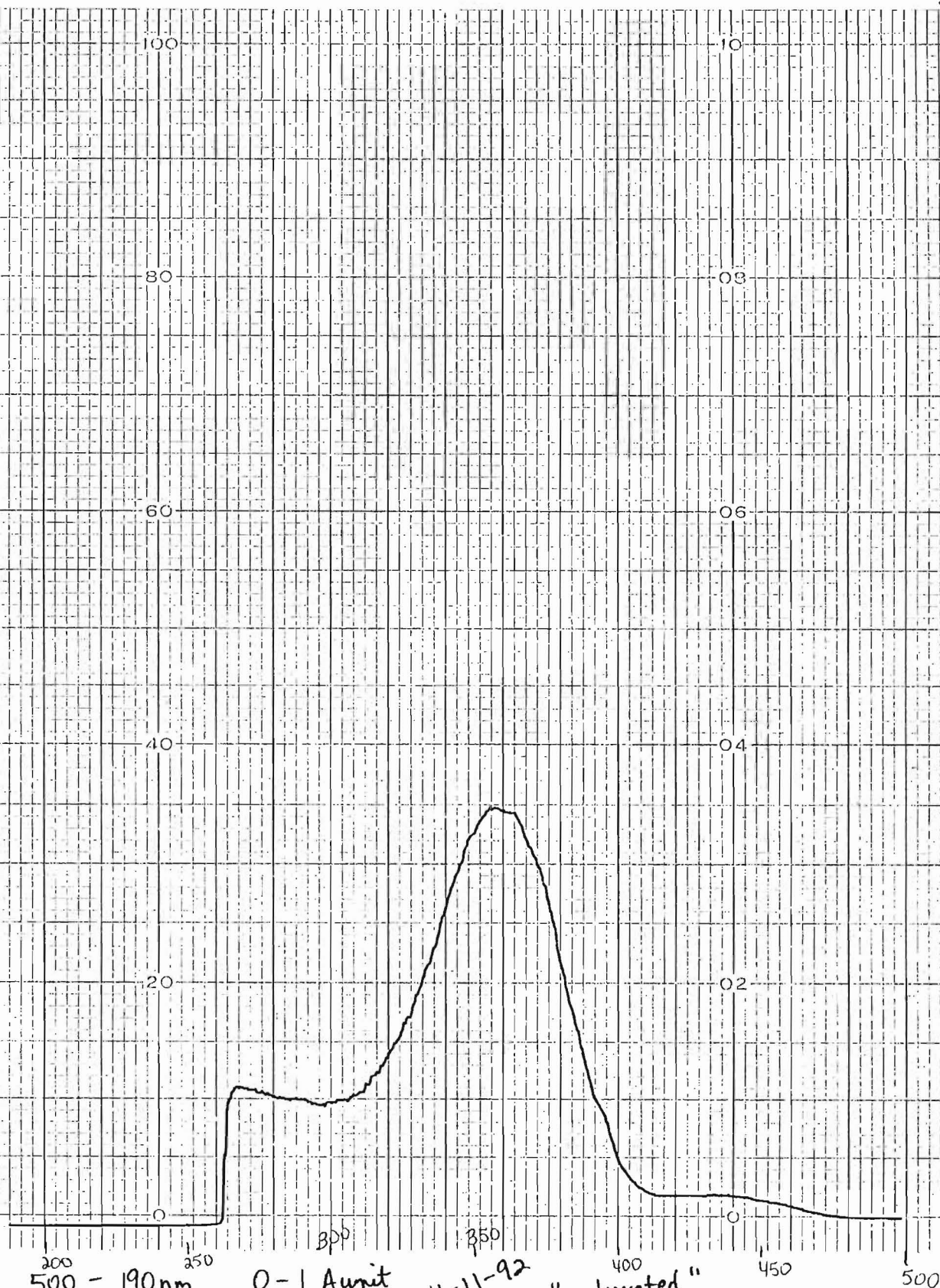
500

450



S #11

S#30



500 - 190 nm

60 nm/min

20 cm/min

slit = 1.0 nm

O-1 Aunit

11-11-92

"saturated"  
NaNO<sub>2</sub> in  
"wet" DMF

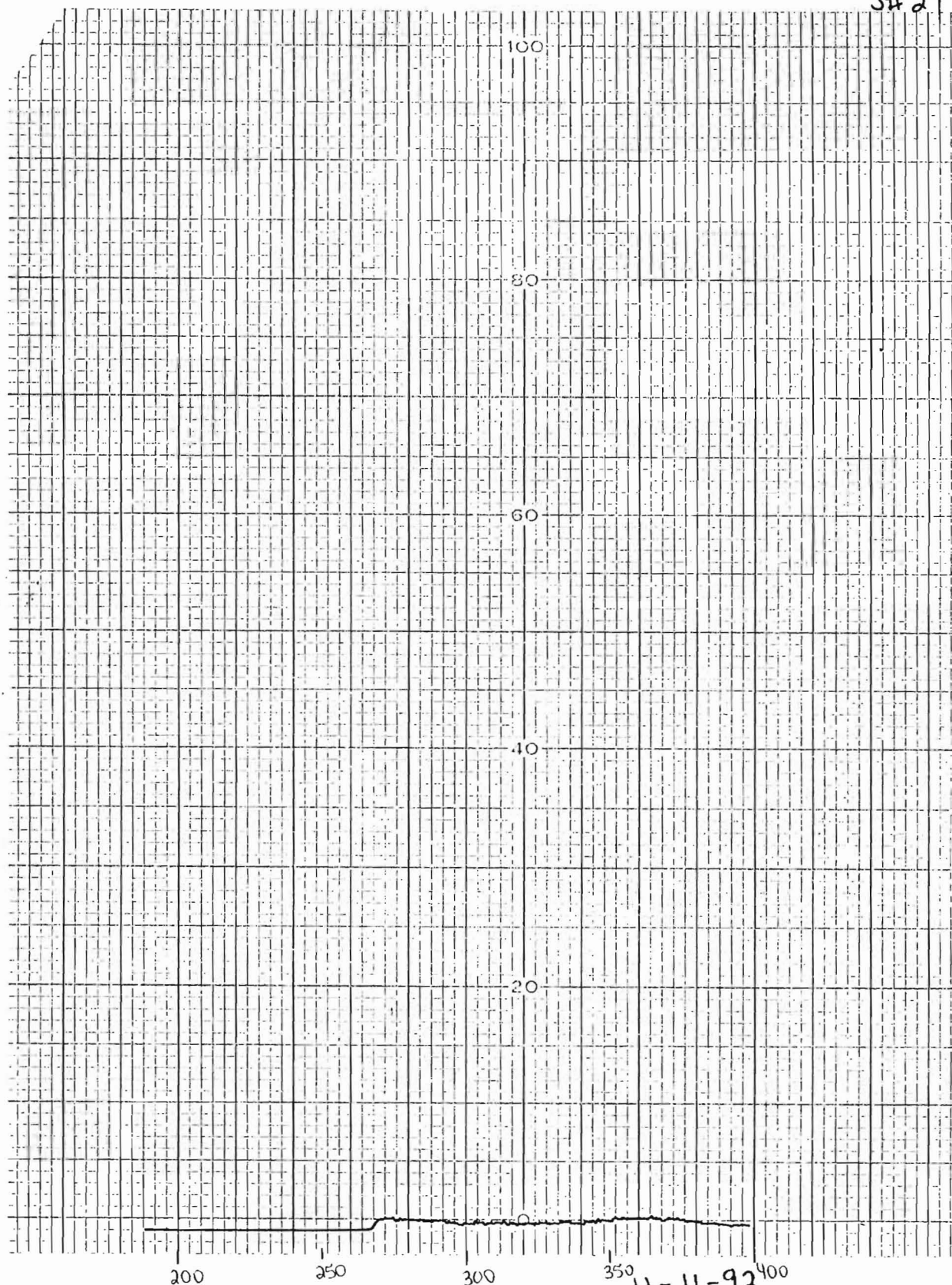
PERKIN ELMER

PART NO. B009392

A29



S# 27



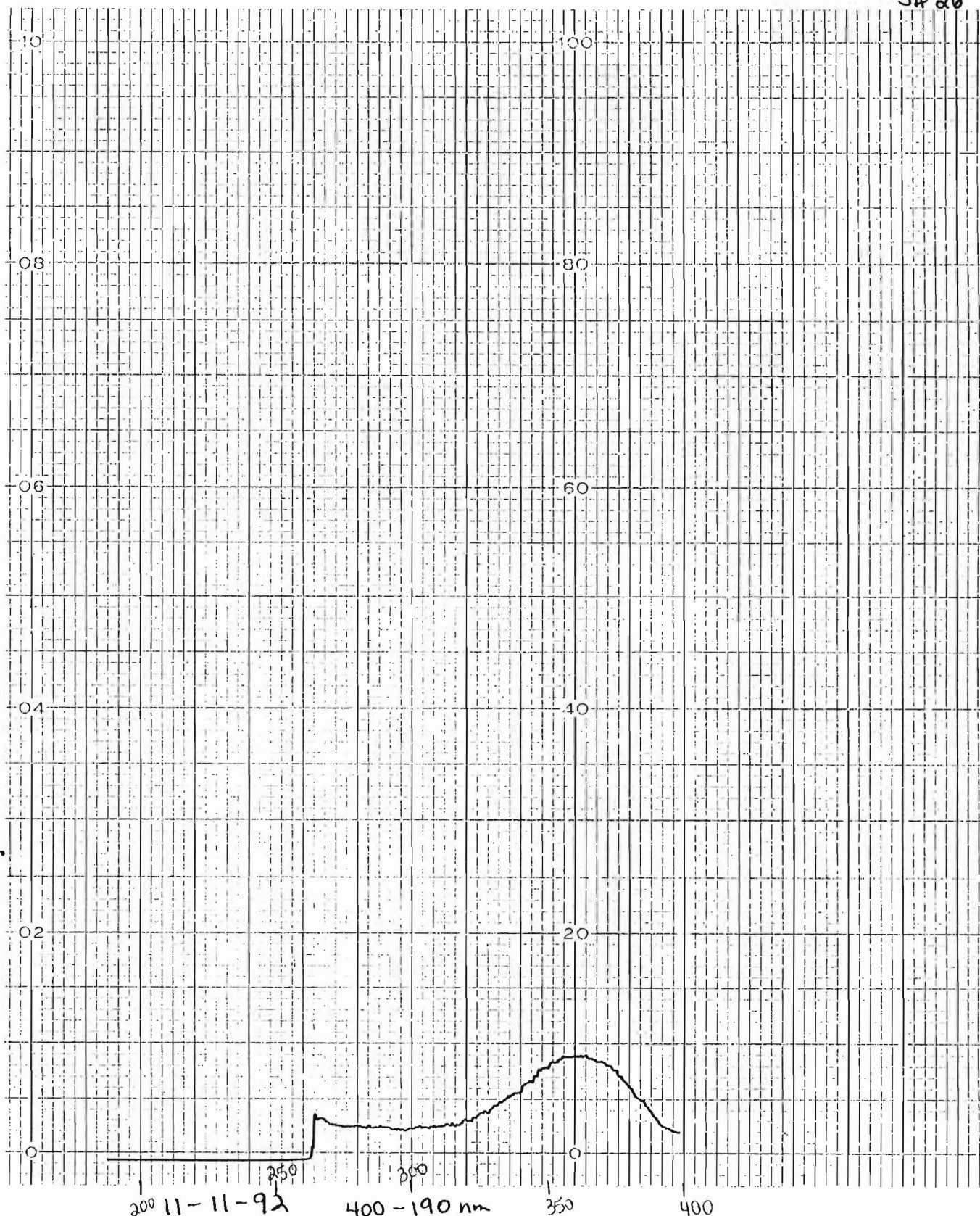
400-190 nm  
60 nm/min  
20 cm/min  
Slit = 1.0 nm

0-1 Aunit

11-11-92

$2.0 \times 10^{-3}$  M  $\text{NaNO}_2$   
in DMF

S# 26



200 11-11-92

400-190 nm  
60 nm/min  
20 cm/min  
slit = 1.0 nm

$2.8 \times 10^{-3} \text{ M}$  NaNO2  
in DMF

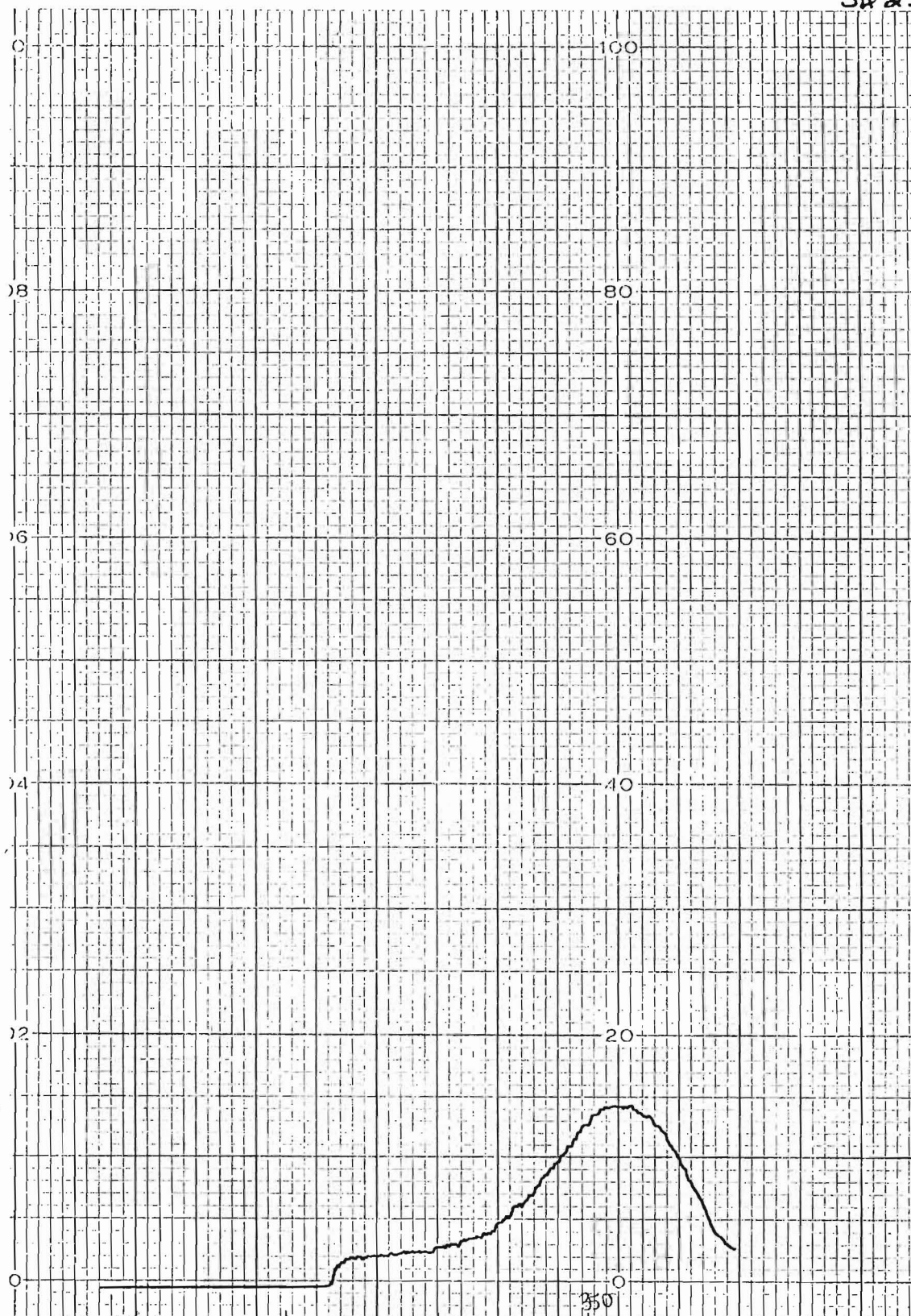
0-1 A unit

PART NO. B0093925

PERKIN ELMER

A31

St# 25



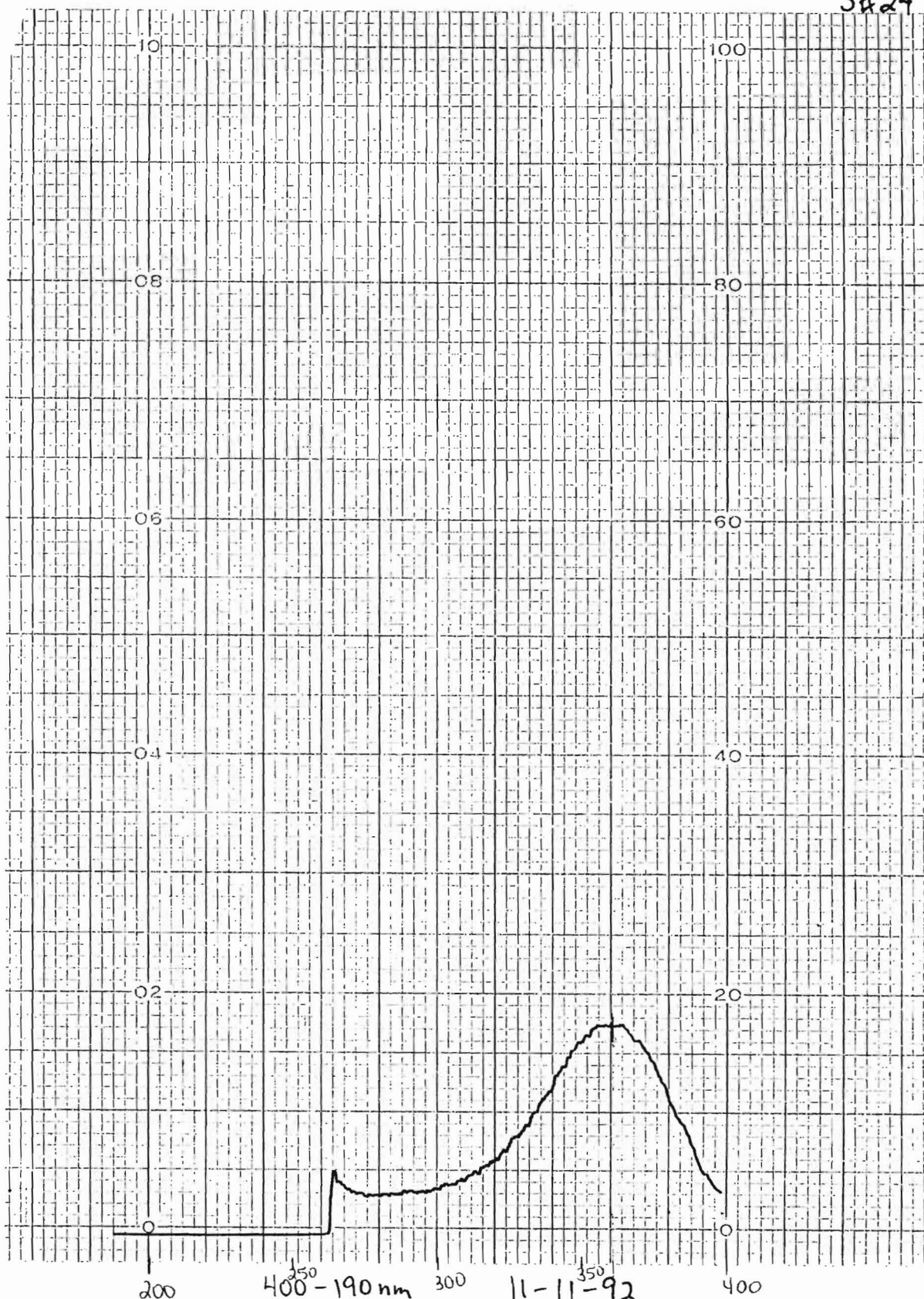
300 250 300  
400 - 190 nm 0-1 A unit  
60 nm/min  
20 cm/min  
slit = 1.0 nm

11-11-92 400

$5.8 \times 10^{-3} \text{ M NaNO}_2$   
in DMF



S#24



400-190 nm  
60 nm/min  
20 cm/min  
slit = 1.0 nm  
0-1 A unit

11-11-92

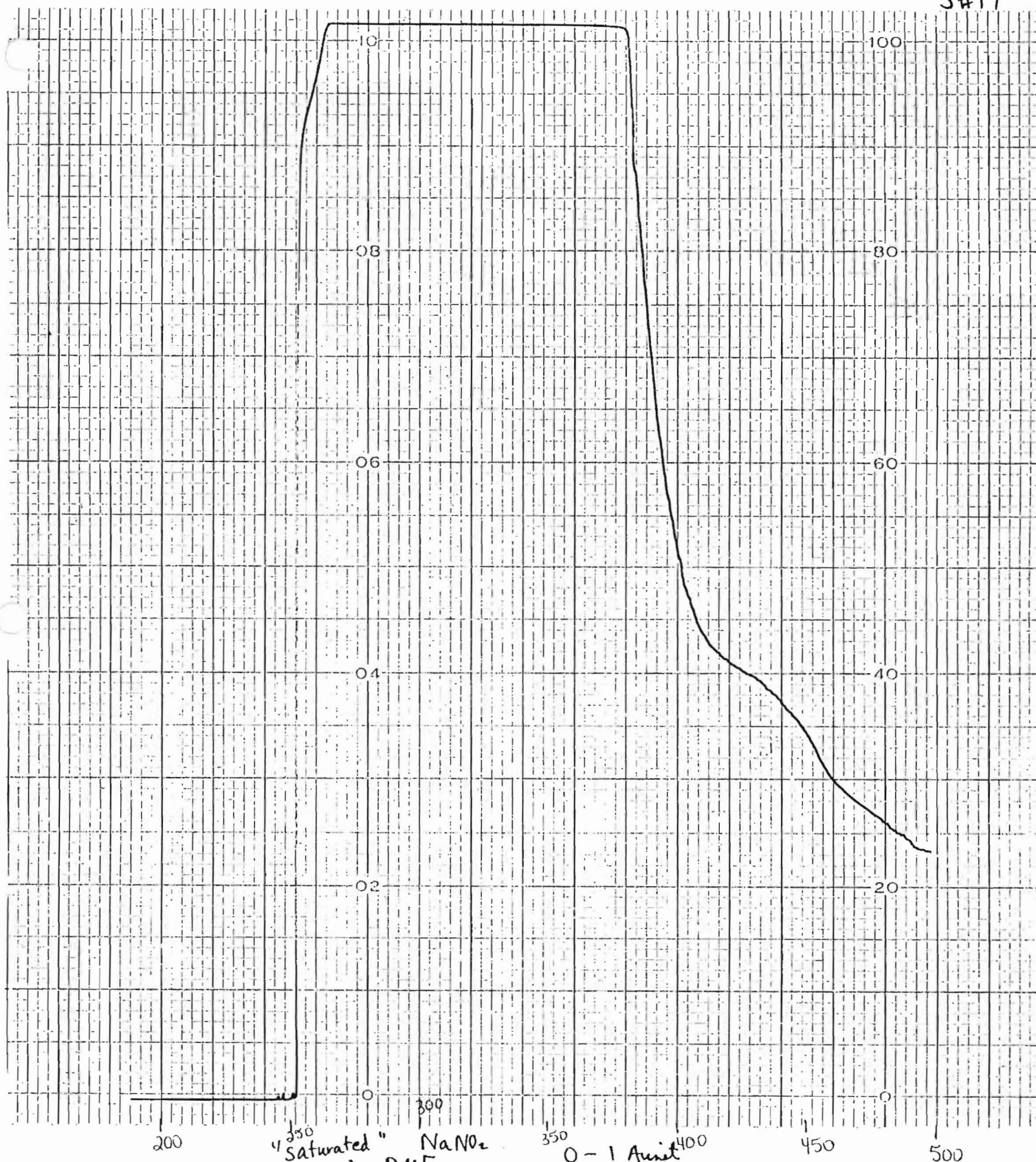
$8.5 \times 10^{-3} \text{ M NaNO}_2$   
in DMF

PART NO. B0093925

PERKIN ELMER

A33

S#17



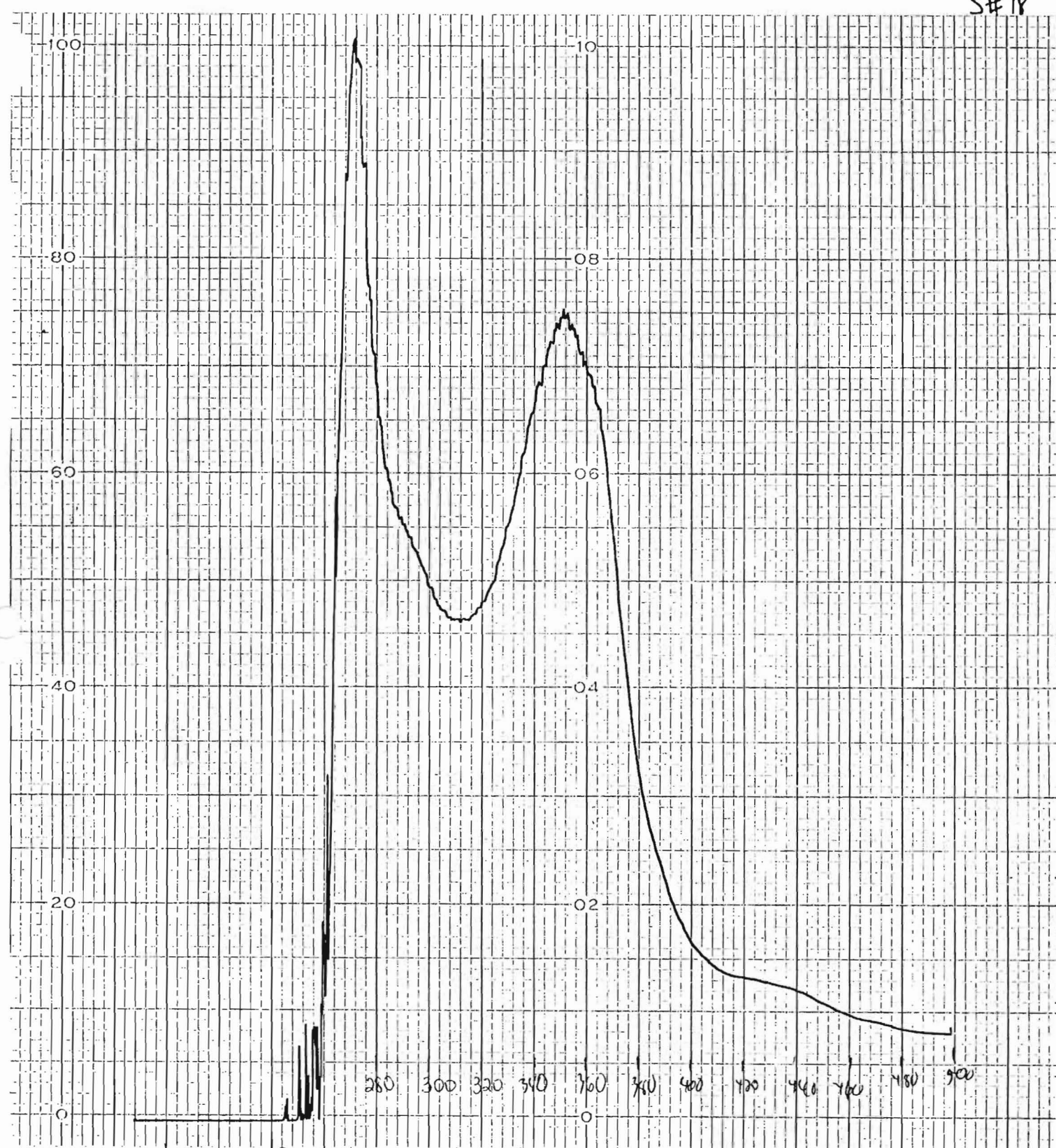
"Saturated"  $\text{NaNO}_2$   
in DMF  
thermolyzed

0 - 1 A unit  
500 - 190 nm  
20 cm/min  
60 nm/min

Slit = 1.0 nm



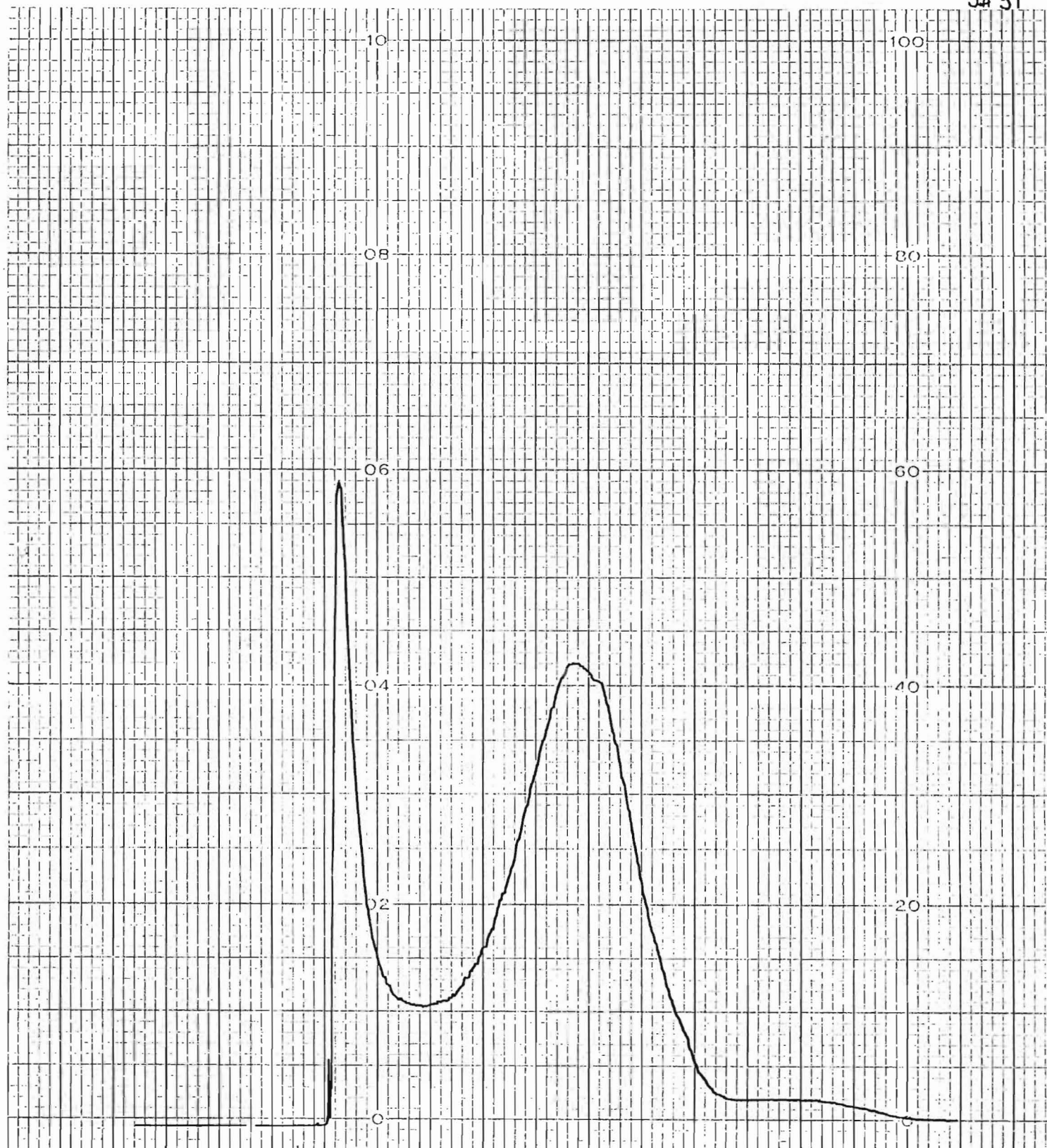
S# 18



200 220 240 260  
 "saturated"  $\text{NaNO}_2$   
 in DMF  
 thermolyzed

0 - 3 A units  
 500 - 190 nm  
 20 cm/min  
 60 nm/min

slit = 1.0 nm



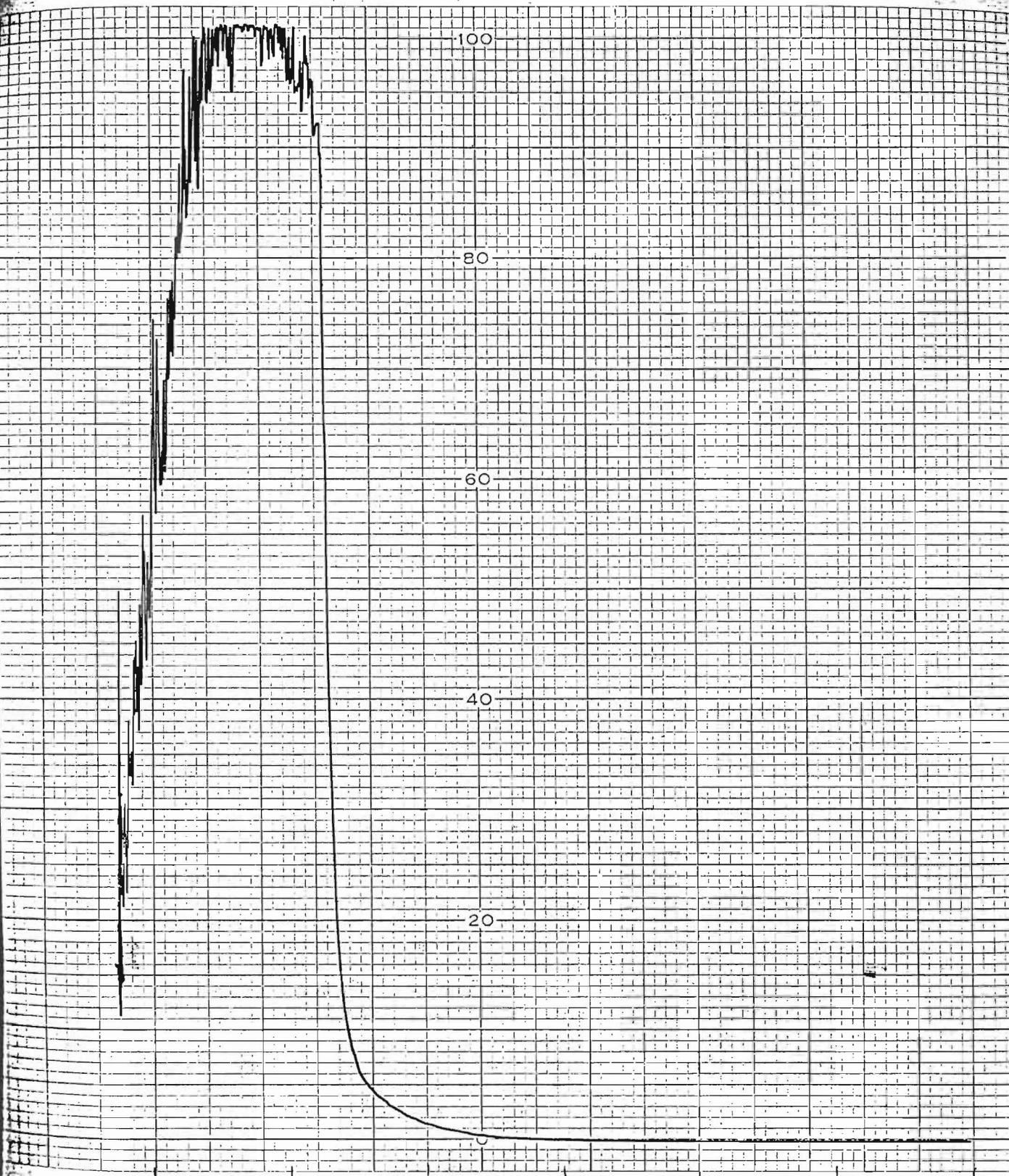
200 250  
500-190 nm  
60 nm/min  
20 cm/min  
slit= 1.0 nm  
0-1 A unit

"saturated"  $\text{NaNO}_2$   
in "wet" DMF  
thermolyzed

400 420 440 460 480  
11-11-92







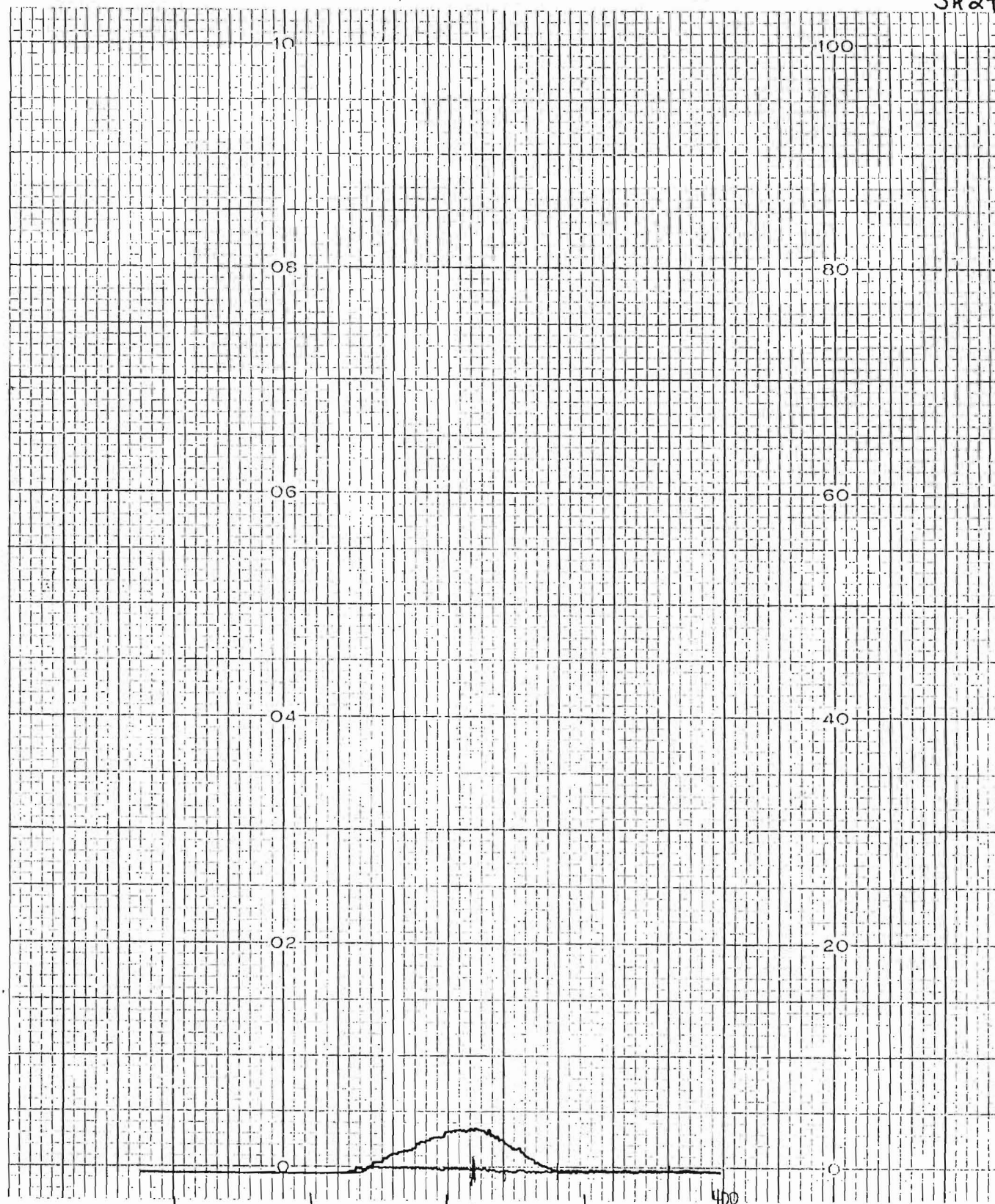
S# 22

thermolysis of  
"wet" DMF

0-3 Aumit  
500-190nm

60 nm/min  
20 nm/cm  
slit = 1.0nm

S#29



11-11-92

0: "saturated"  $\text{NaNO}_3$   
in DMF

400-190 nm  
60 nm/min  
20 cm/min  
slit = 1.00 nm

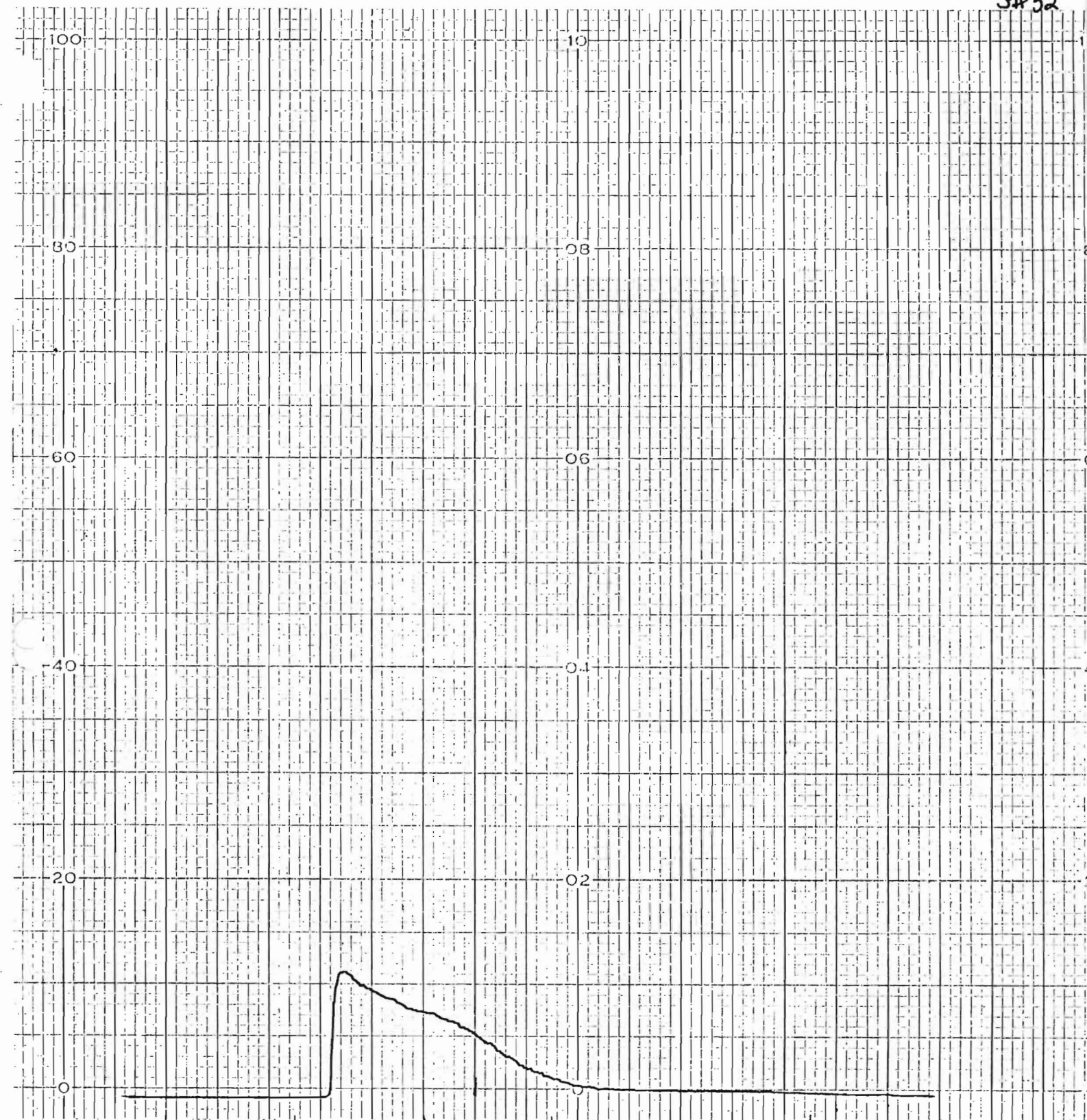
0 - 1 Aunit

PART NO. B0093925

PERKIN EL

A39

SH 32



200  
500 - 190 nm  
60 nm/min  
20 cm/min  
Slit = 1.0 nm

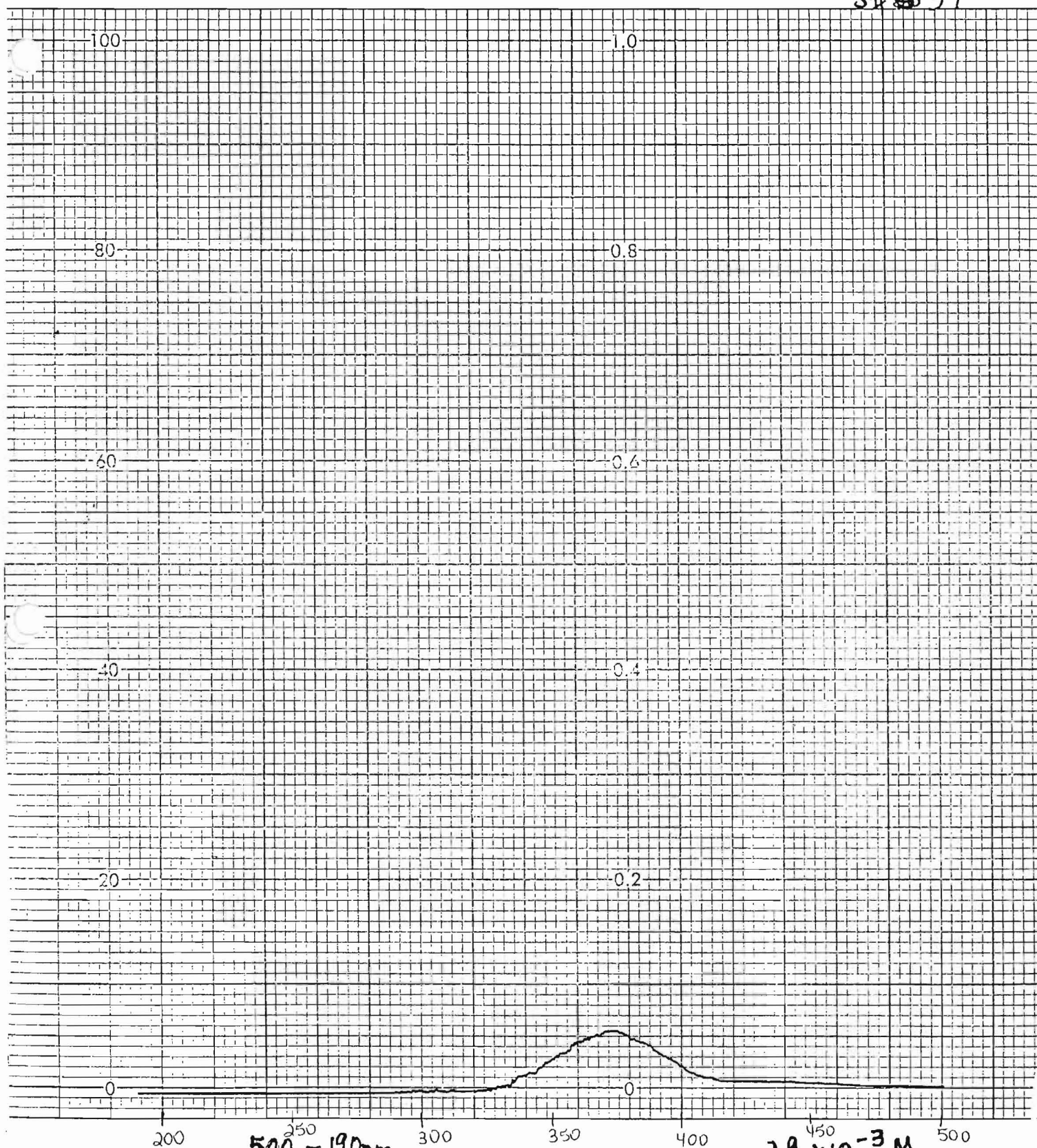
0 - 1 A unit

11-11-92

"Saturated"  $\text{NaNO}_3$   
in "wet" DMF -  
thermolyzed



S# 37



500 - 190 nm

60 nm/min  
20 cm/min  
Slit = 1.0 nm

0 - 1 A unit

$2.9 \times 10^{-3} M$

NaNO<sub>2</sub> in  
DMSO

A41

S#36

100

10

30

03

30

06

40

04

20

02

200

250

300

350

400

450

500

500-190nm

60 nm/min

20 cm/min

slit = 1.0nm

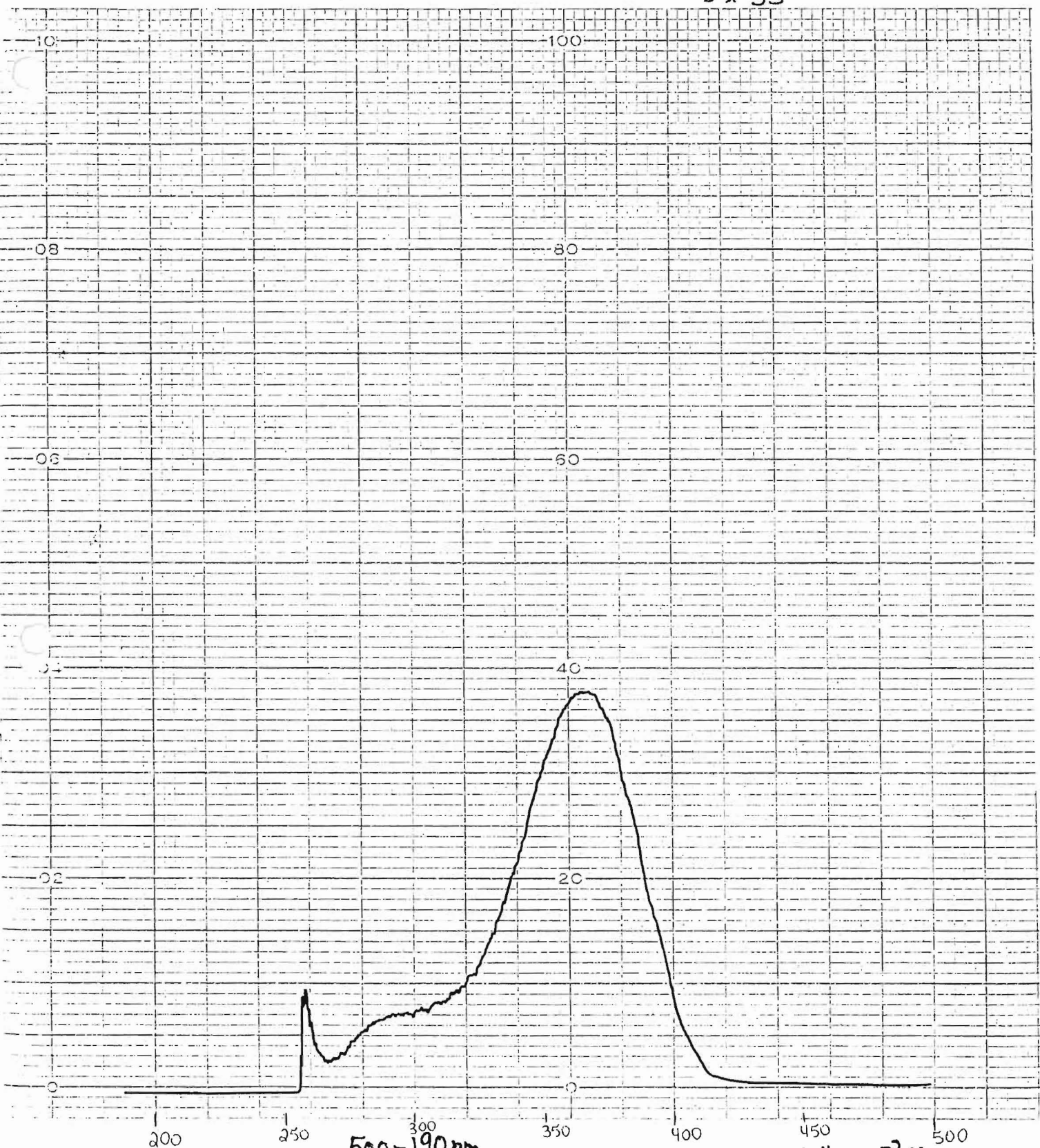
0-1 A unit

$7.0 \times 10^{-3} M$

NaNO<sub>2</sub> in  
DMSO



S# 35

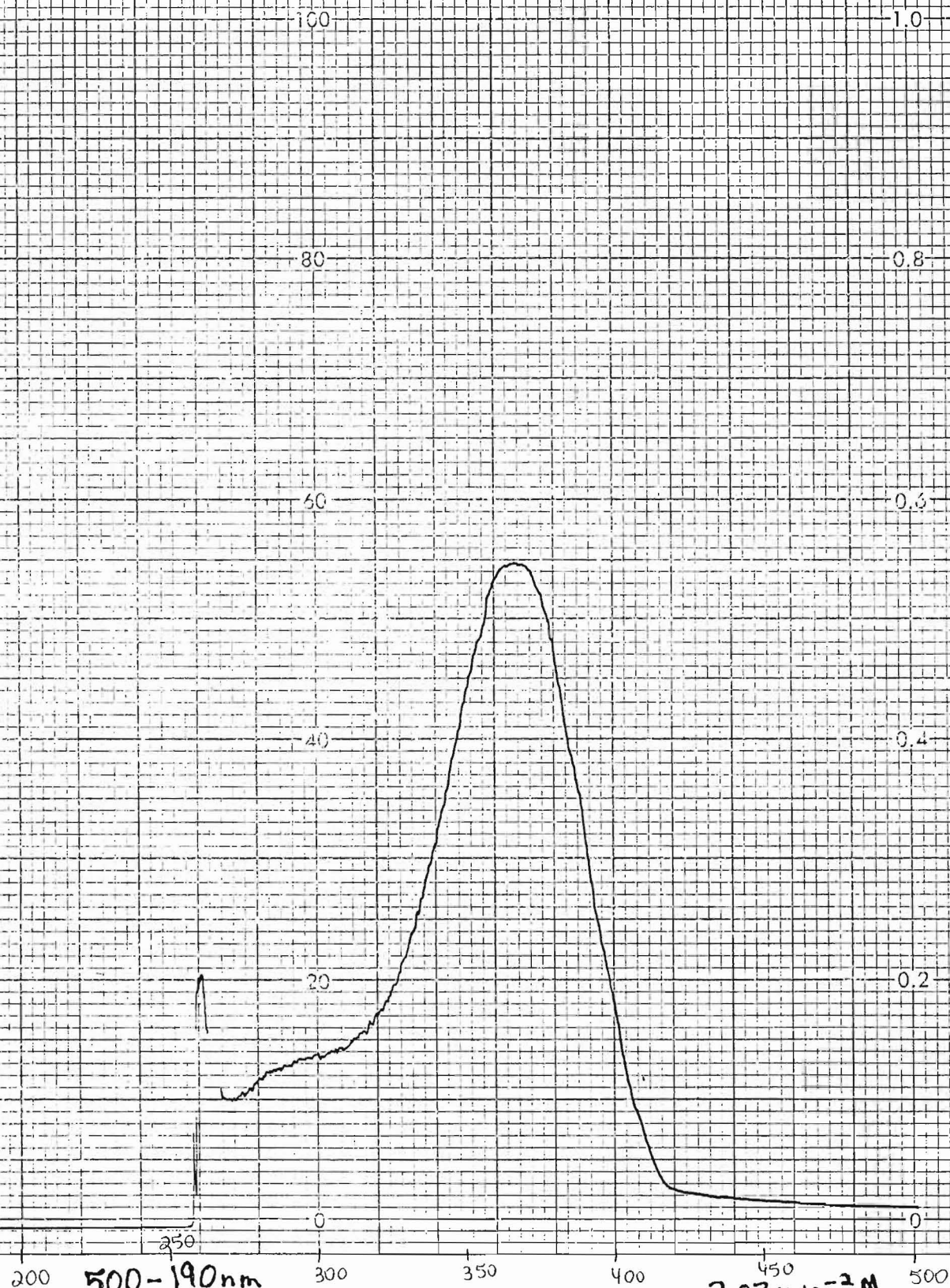


500-190 nm  
60 nm/min  
20 cm/min  
Slit=1.0nm

0-1 A unit

$1.4 \times 10^{-2} M$   
 $NaNO_2$  in  
DMSO

S#34

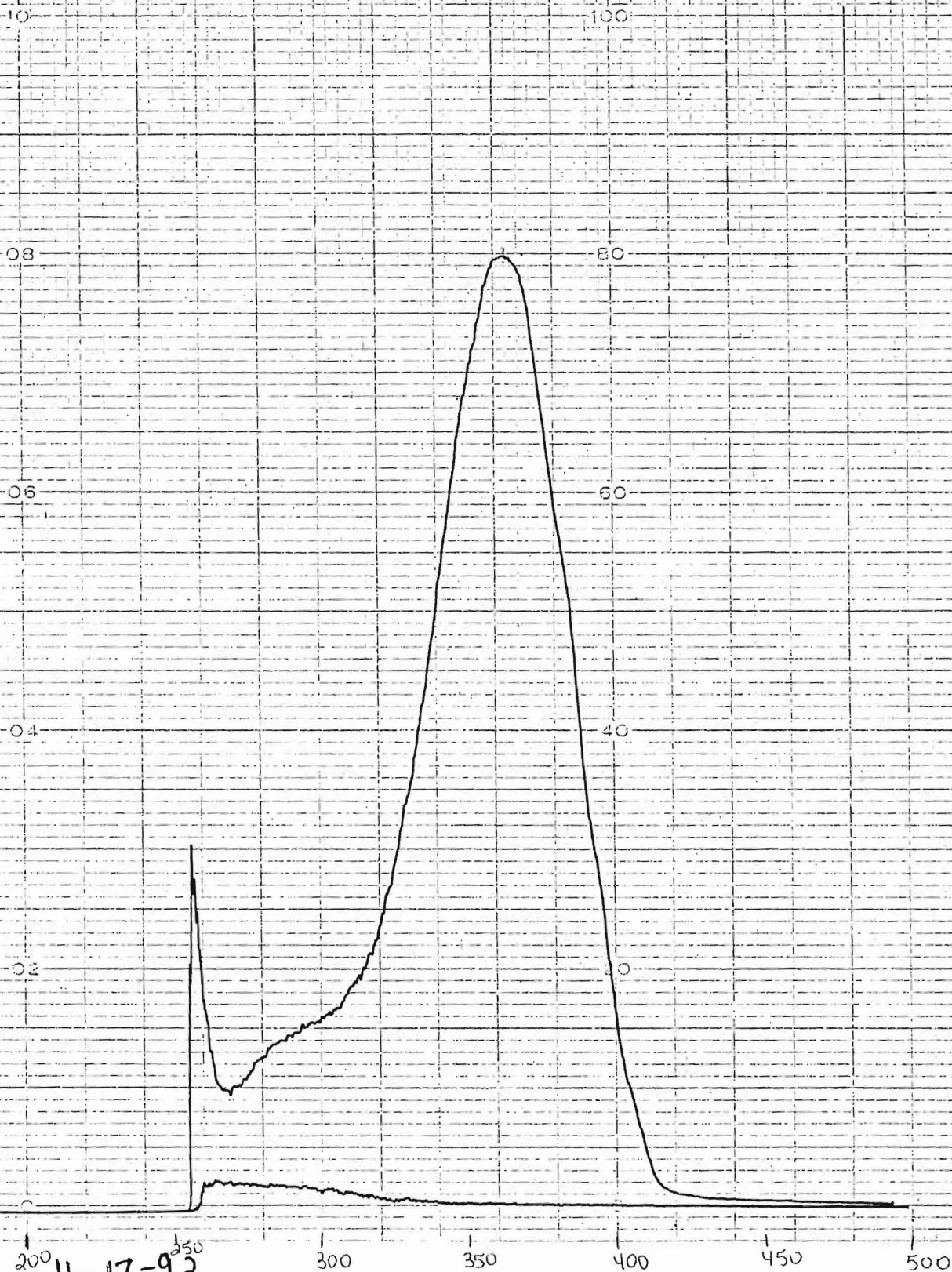


500-190 nm  
60 nm/min  
20 cm/min  
slit = 1.0 nm

0-1 A unit

$2.03 \times 10^{-2} M$   
NaNO<sub>2</sub> in  
DMSO

S# 33



11-17-92

500-190 nm  
60 nm/min  
20 cm/min

slit=1.0 nm  
0-1 Aunit

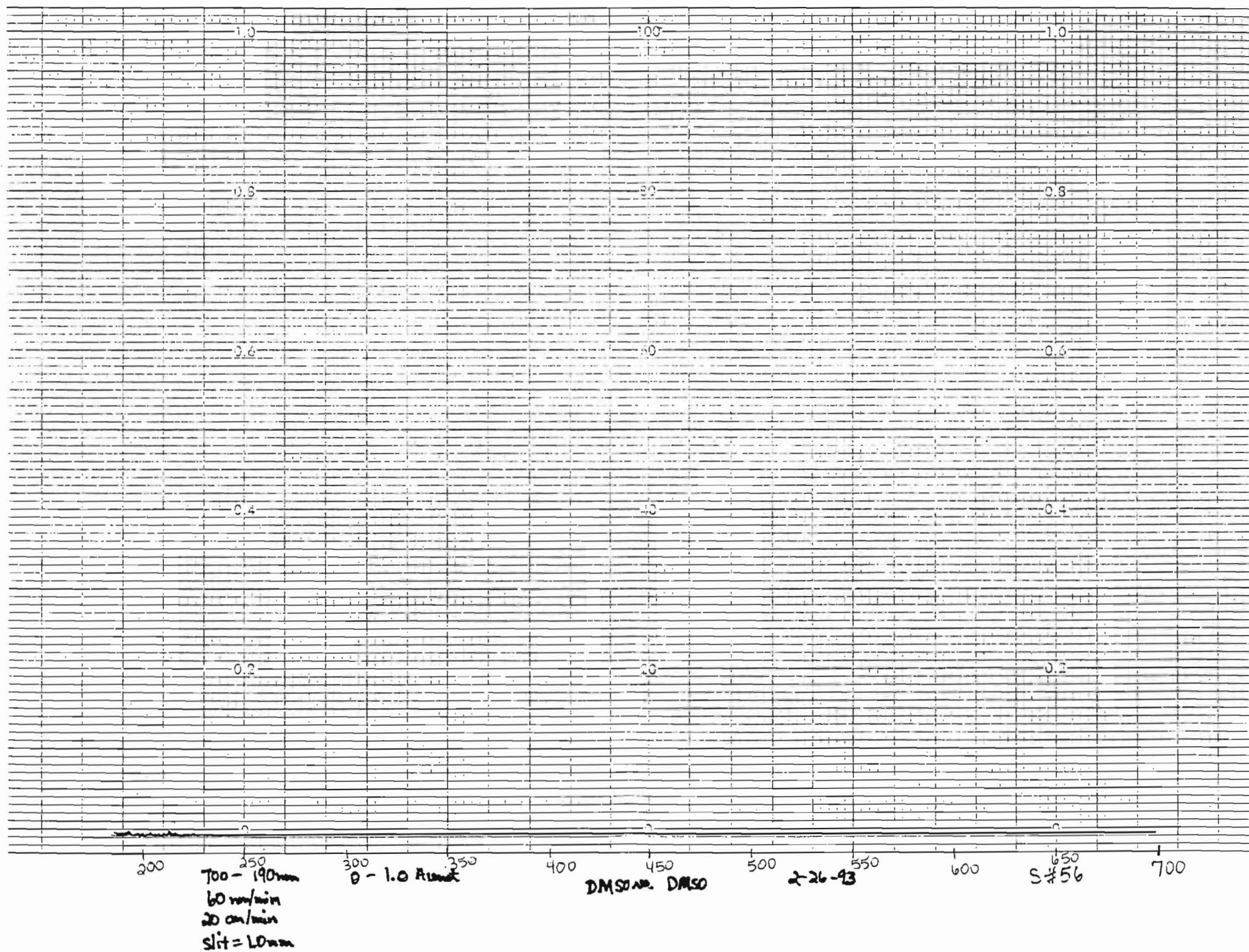
0.0201 g  $\text{NaNO}_2$   
in DMSO

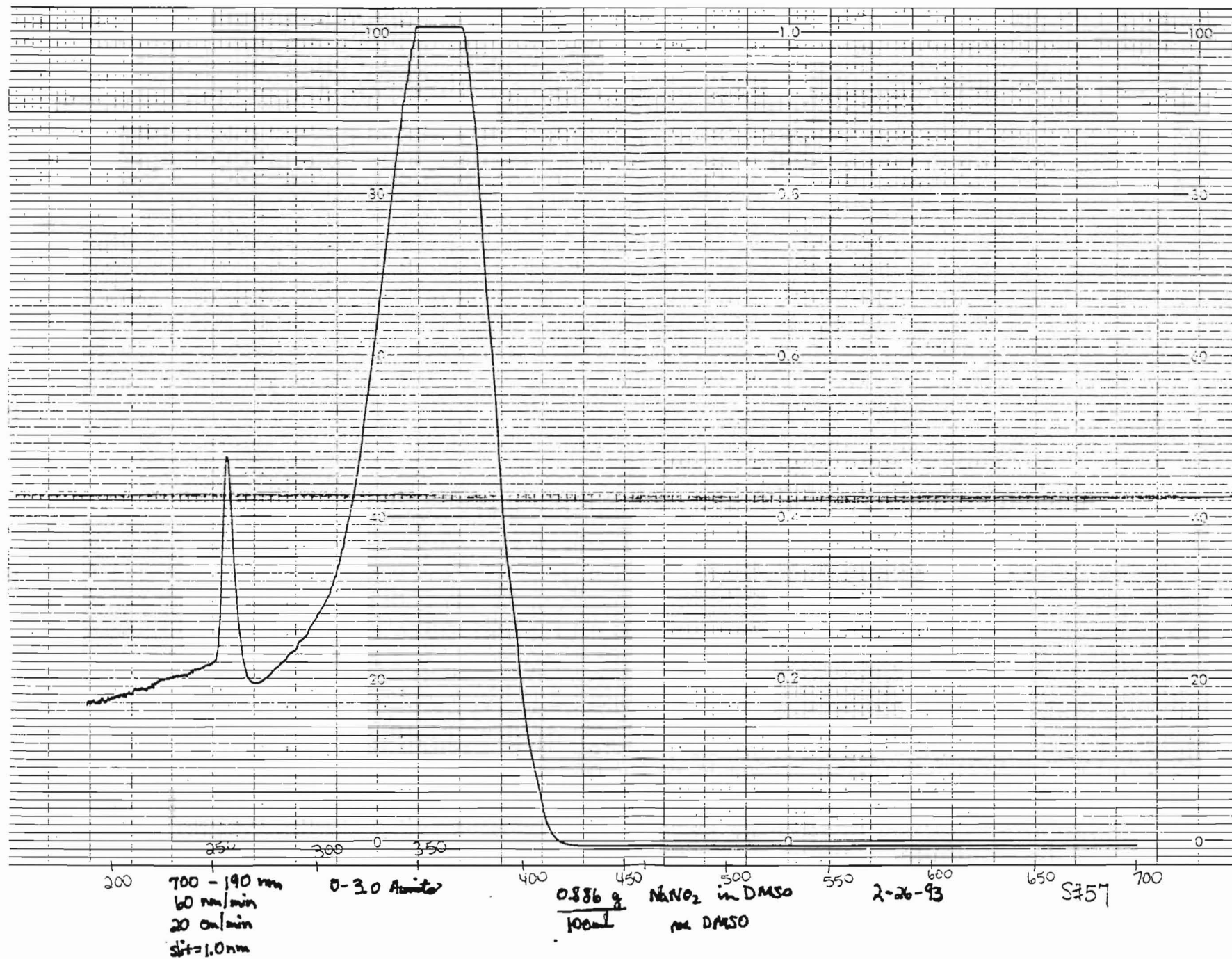
PART NO. BCC93925

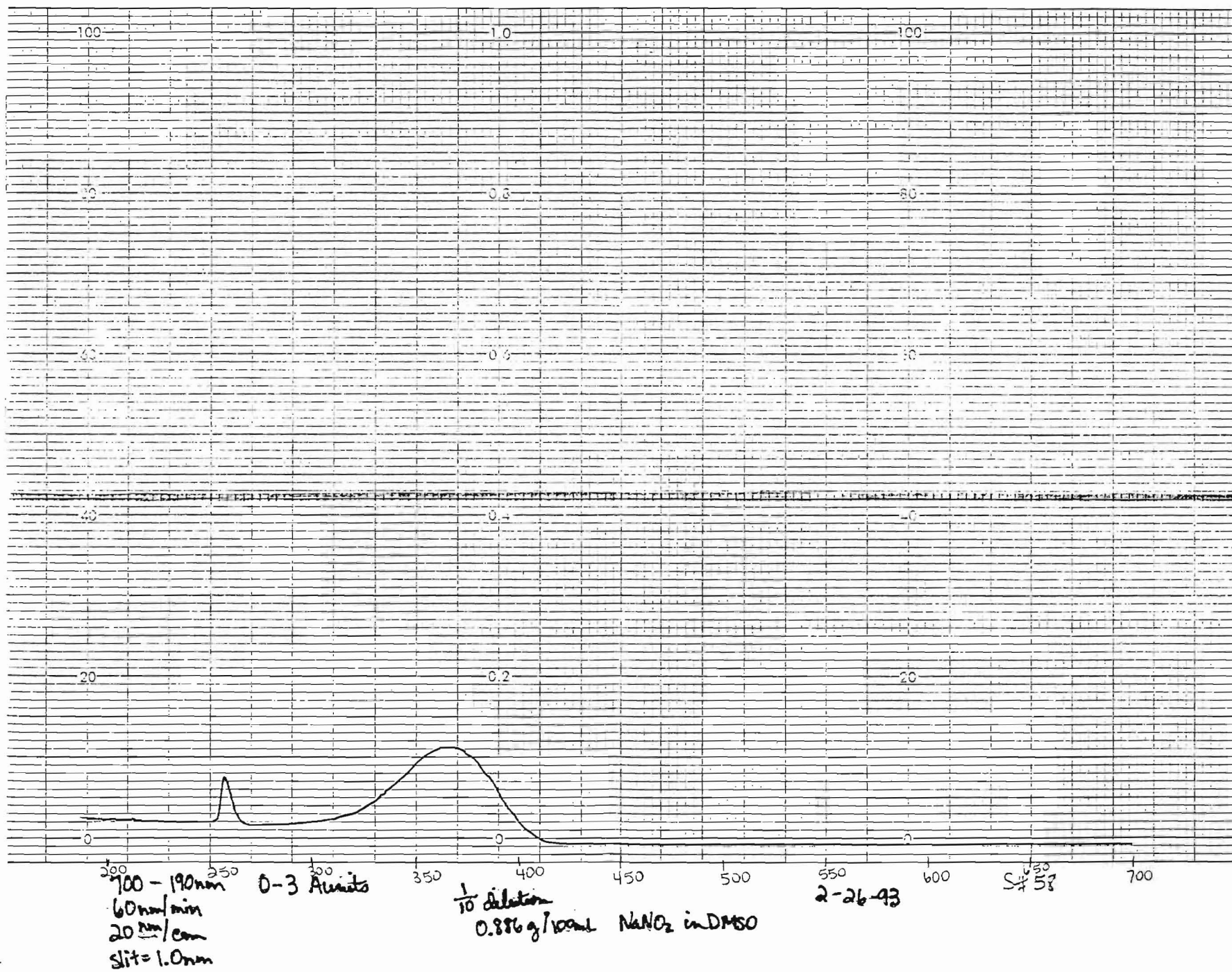
PERKIN-ELMER



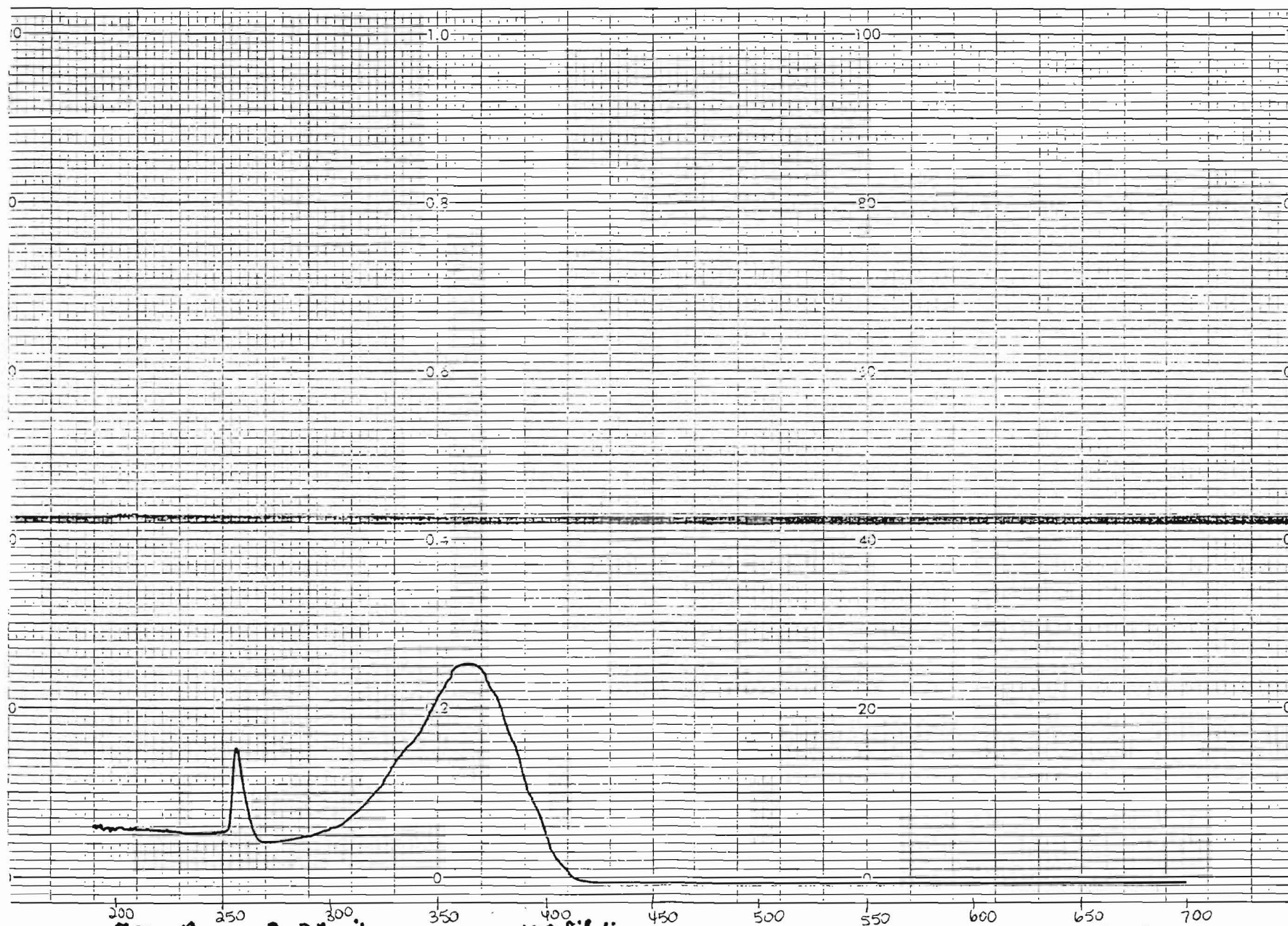
A46











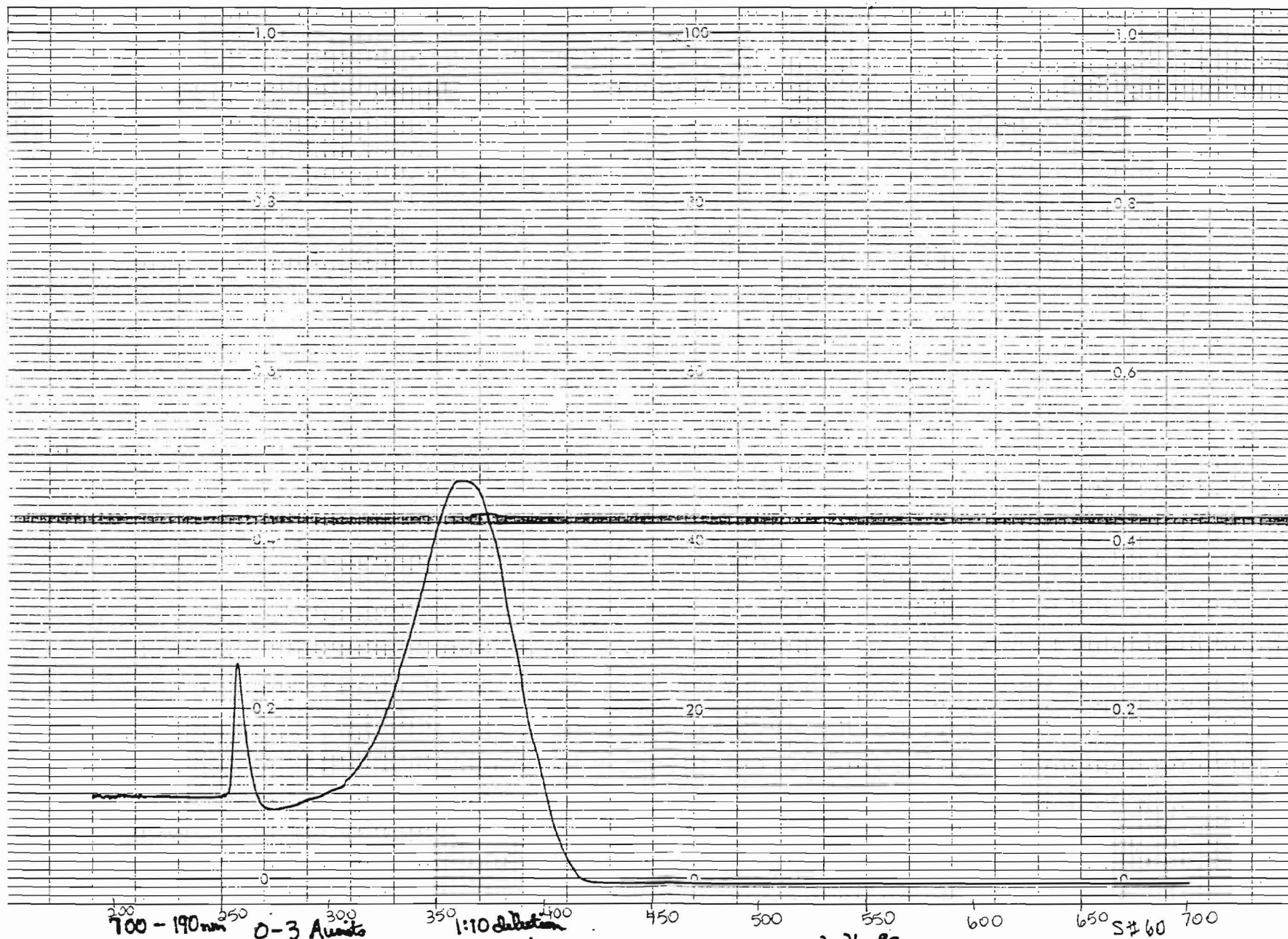
700 - 190 nm  
60 mm/min  
20 mm/cm  
slit = 10 mm

0-3 Accurately

1:10 dilution  
1.880 g/100 ml NaNO<sub>2</sub> in DMSO

2-26-93

S#59



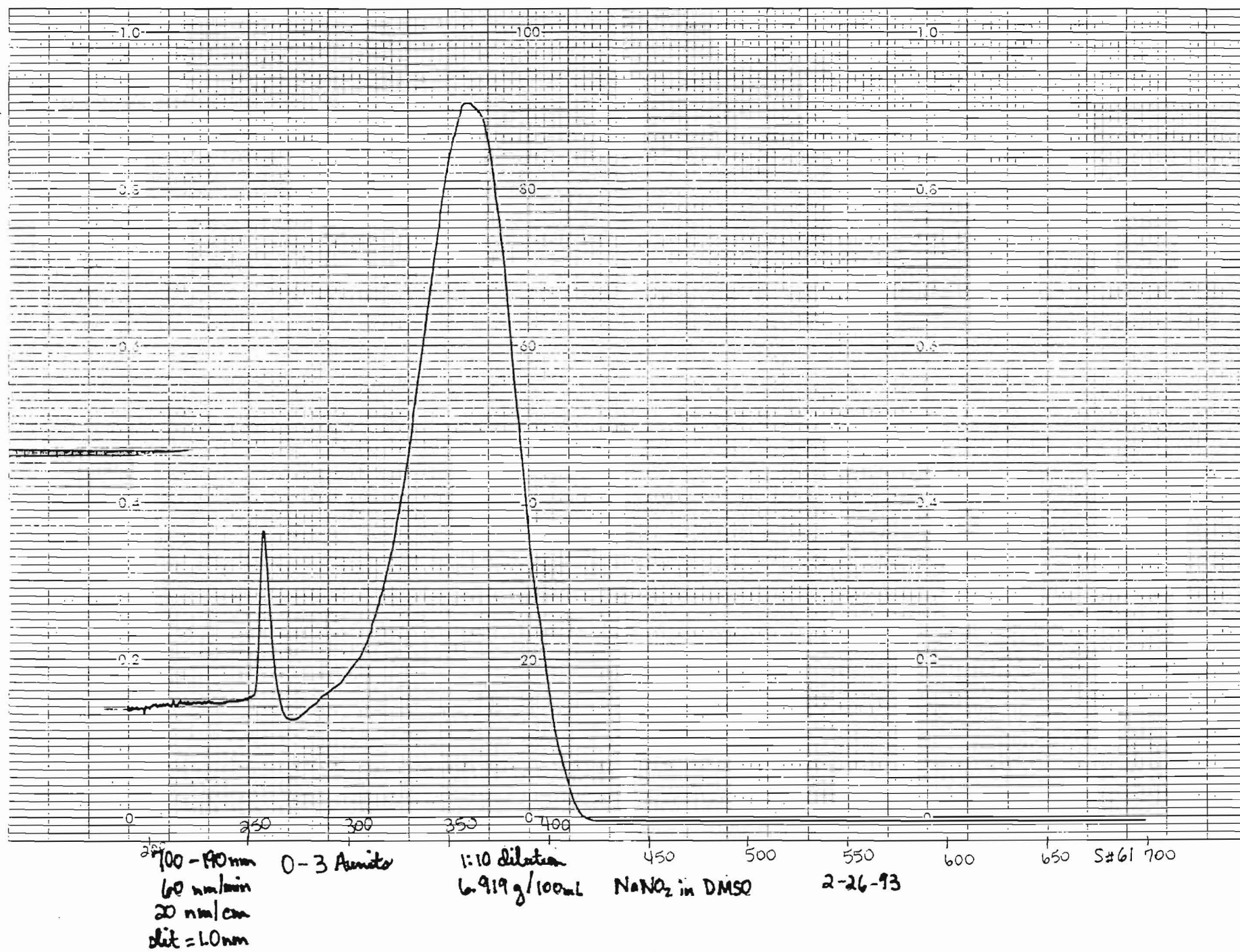
200 250 300 350 400 450 500 550 600 650 700  
700-190 nm  
60 nm/min  
20 nm/cm  
slit = 1.0 nm  
0-3 A units

1:10 dilution  
3.510 g/100 ml NaNO<sub>2</sub> in DMSO

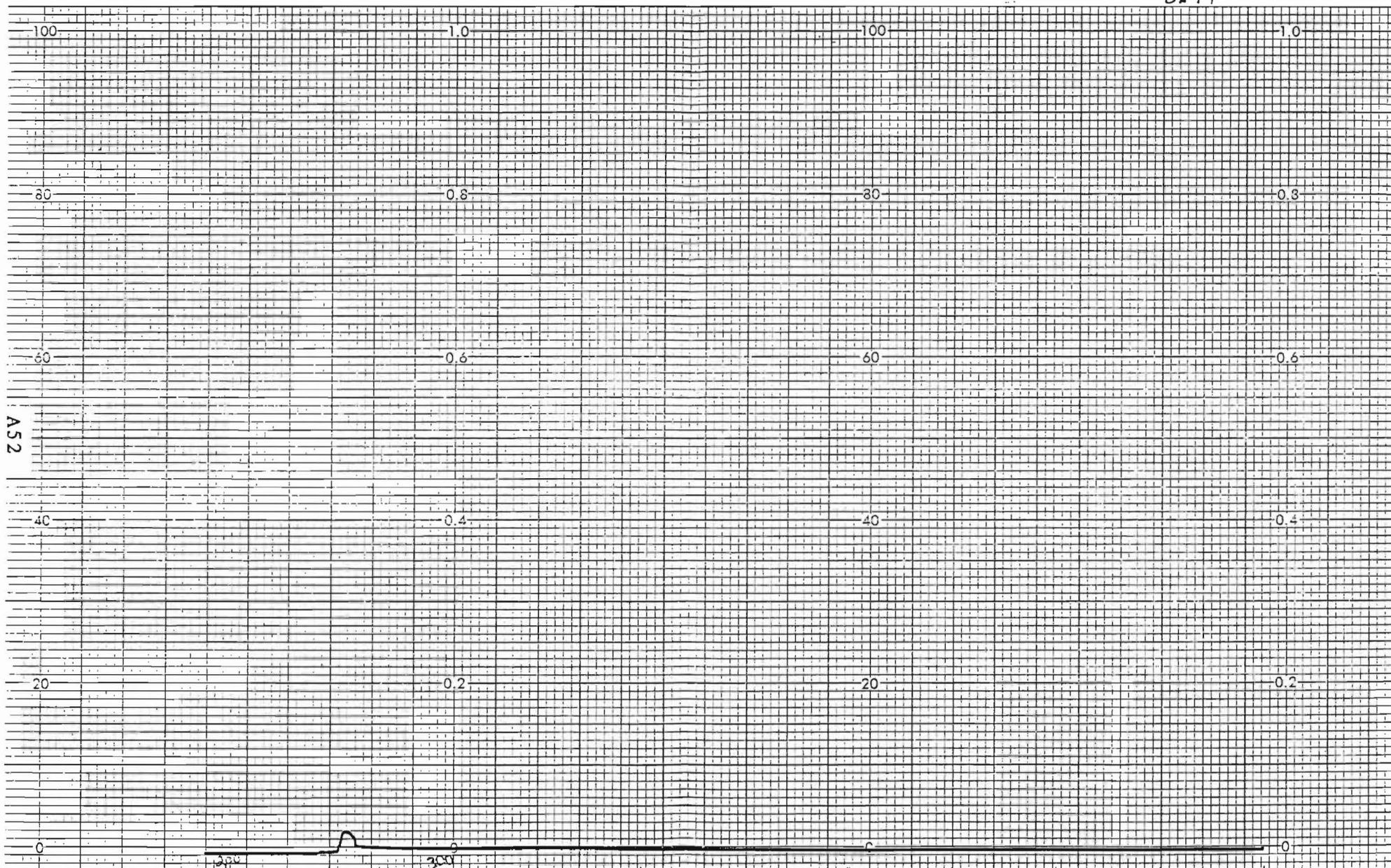
2-26-93

S# 60





S#74



700-190 nm  
60 nm/min  
20 nm/cm  
slit = 1.0 nm

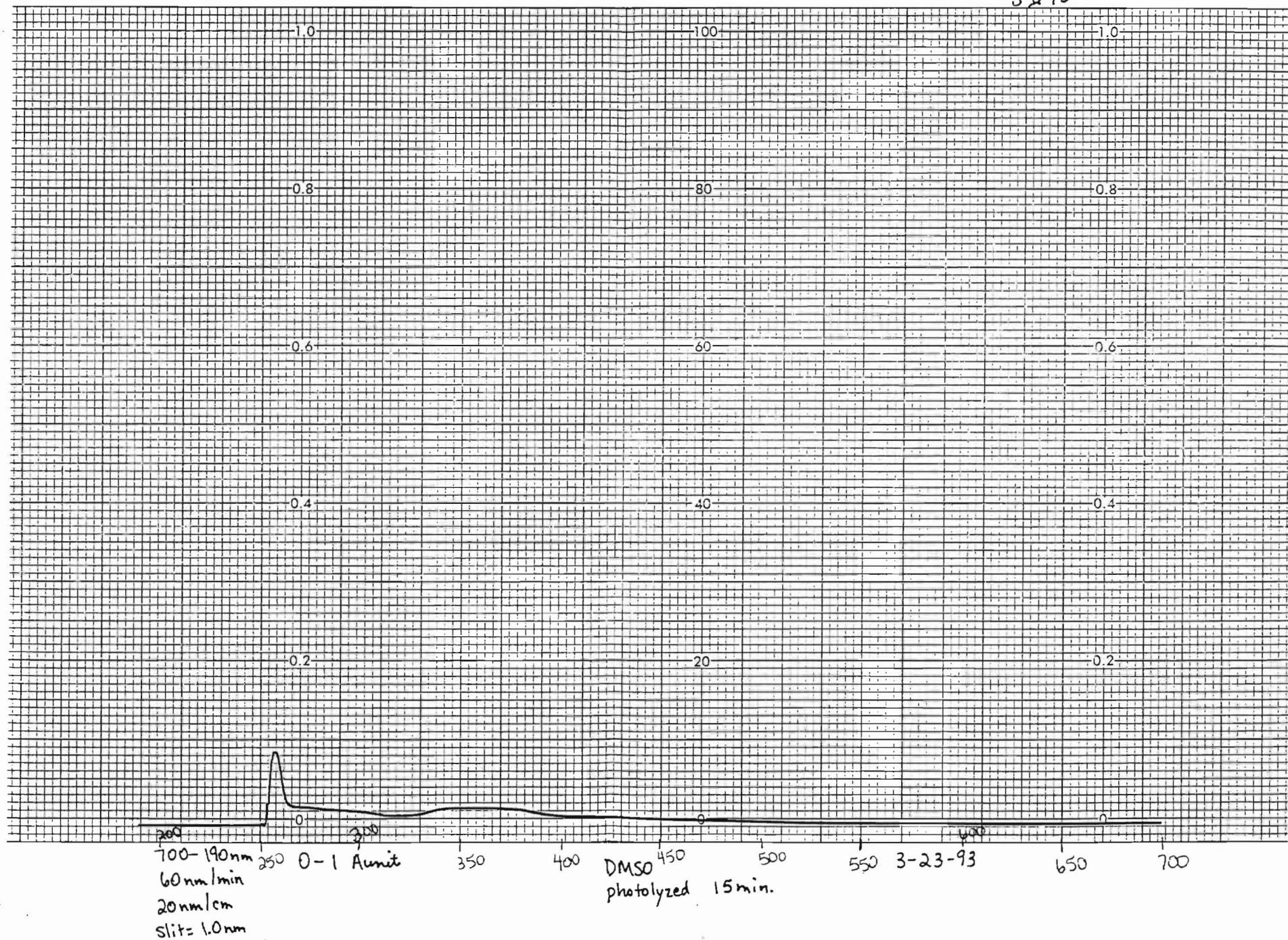
350  
DMSO  
photolyzed 15 min

500 3-23-93

550 600 650 700

S#75

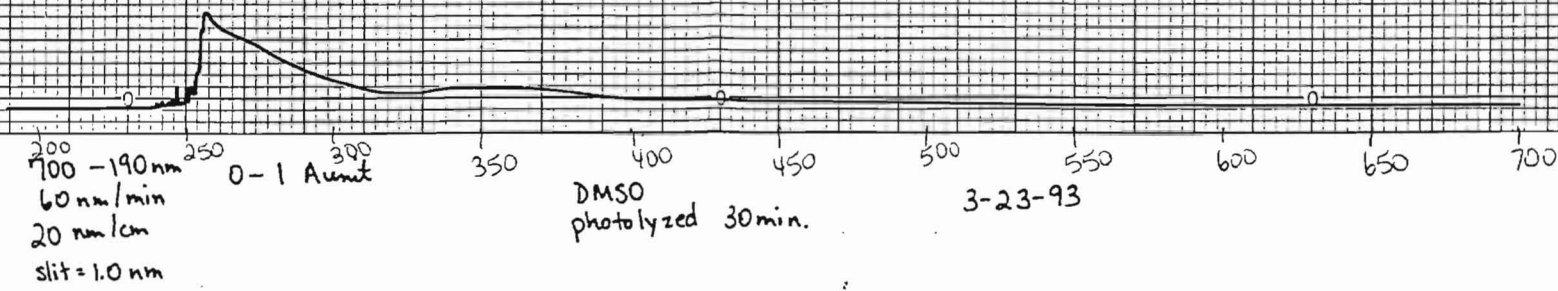
A53





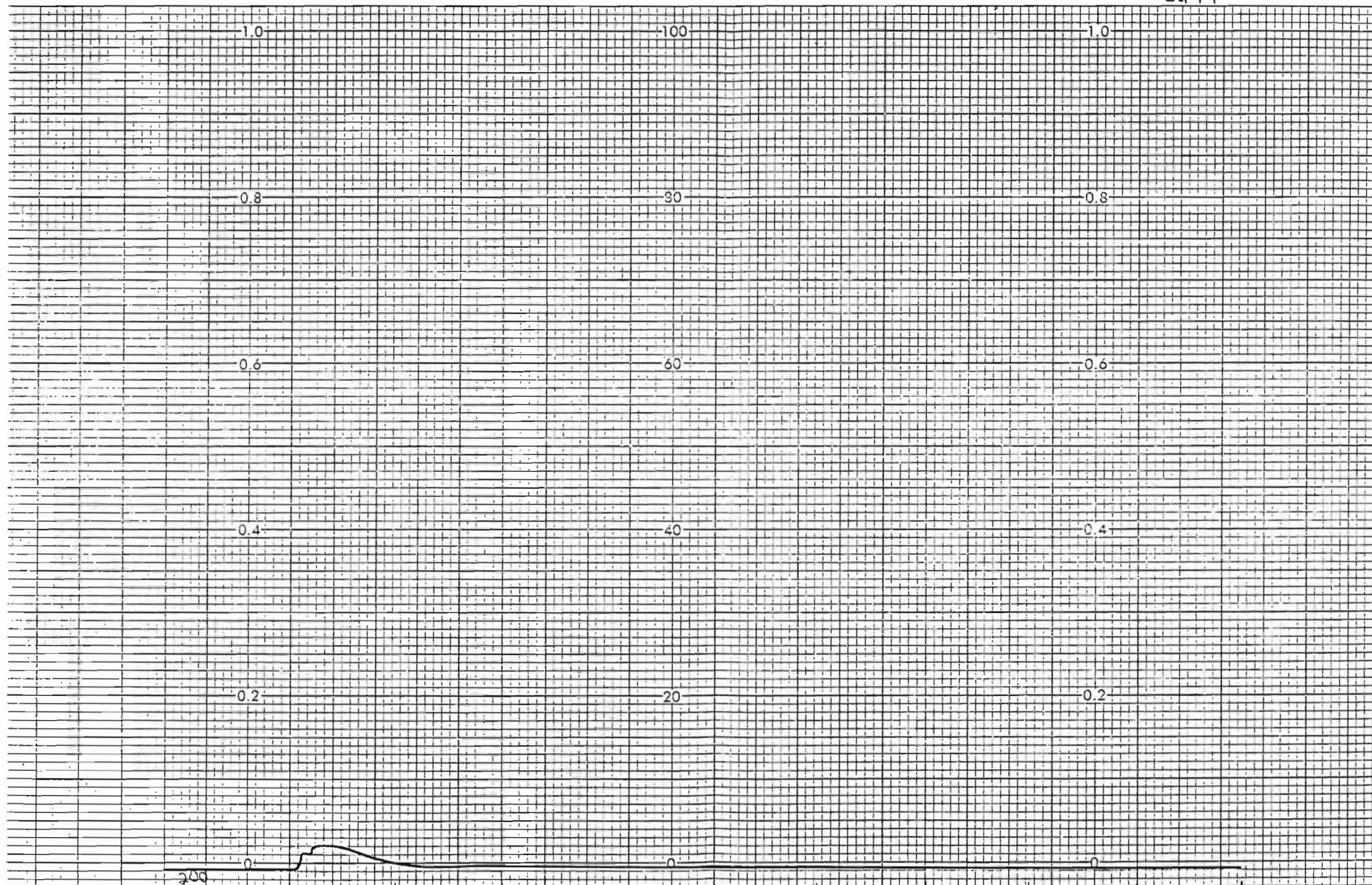
S# 76

AS4



S#77

A55



700 - 190 nm  
60 nm/min  
20 nm/cm  
Slit = 1.0 nm

0 - 1 A unit

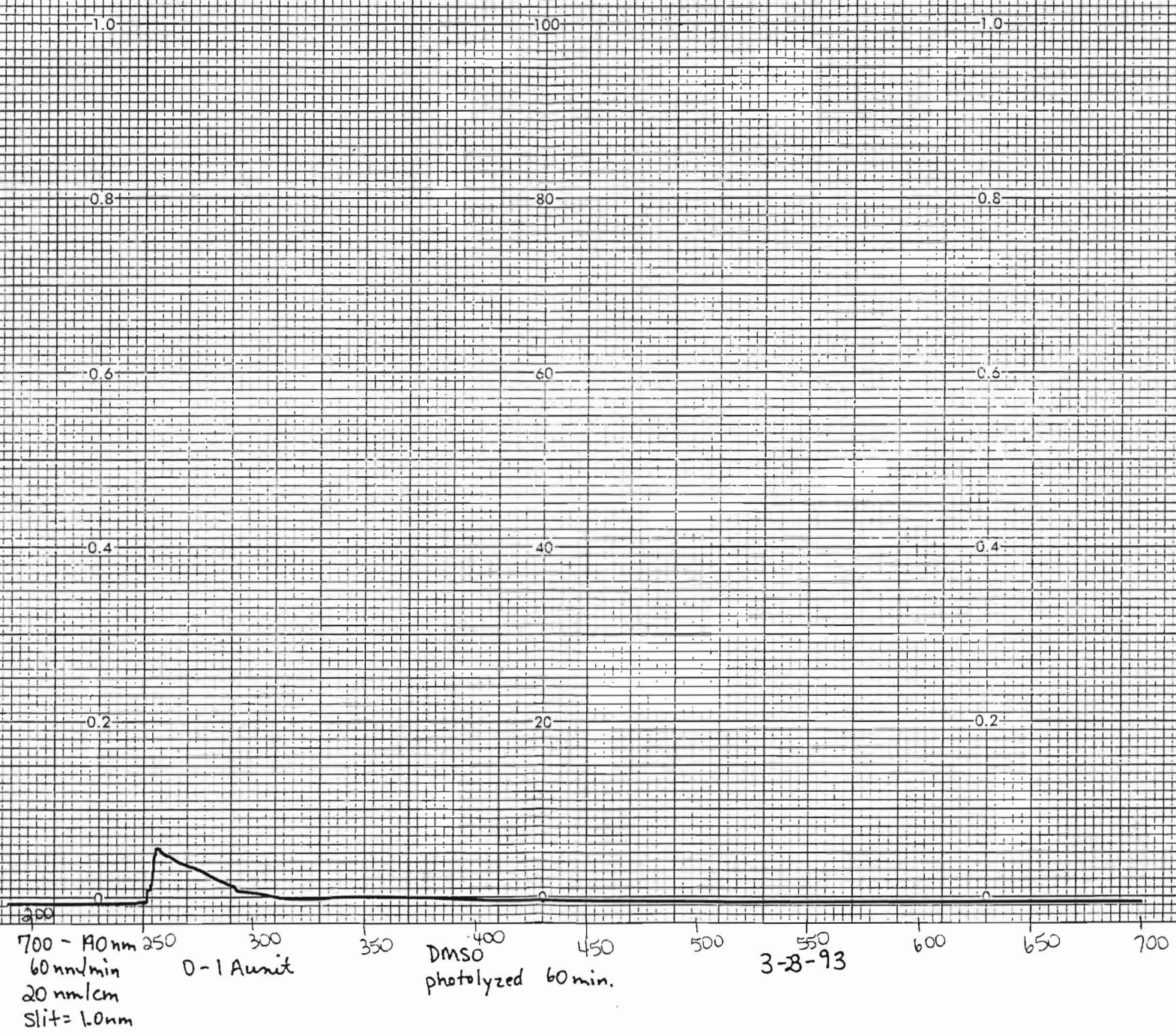
DMSO  
photolyzed 45 min

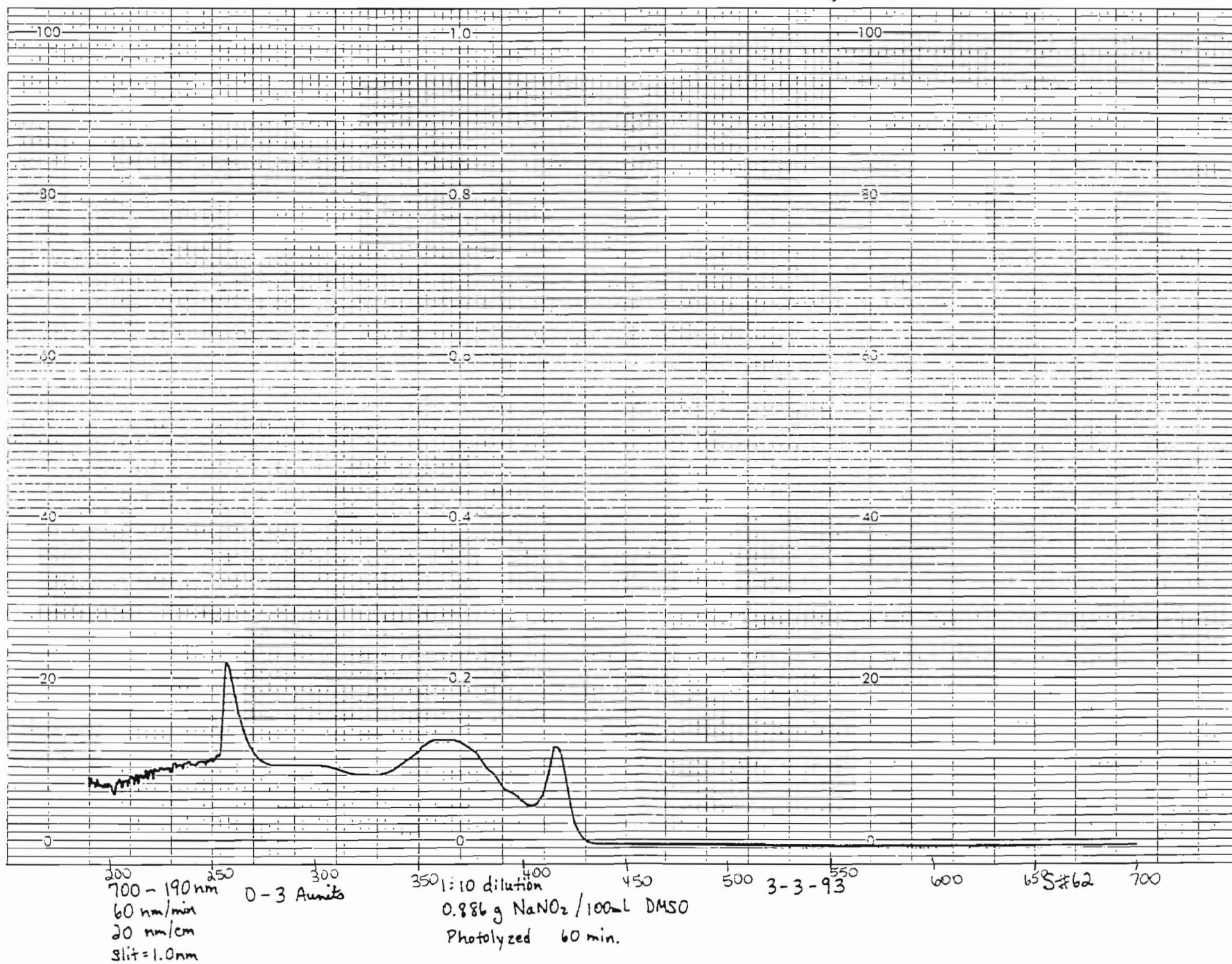
3-23-93



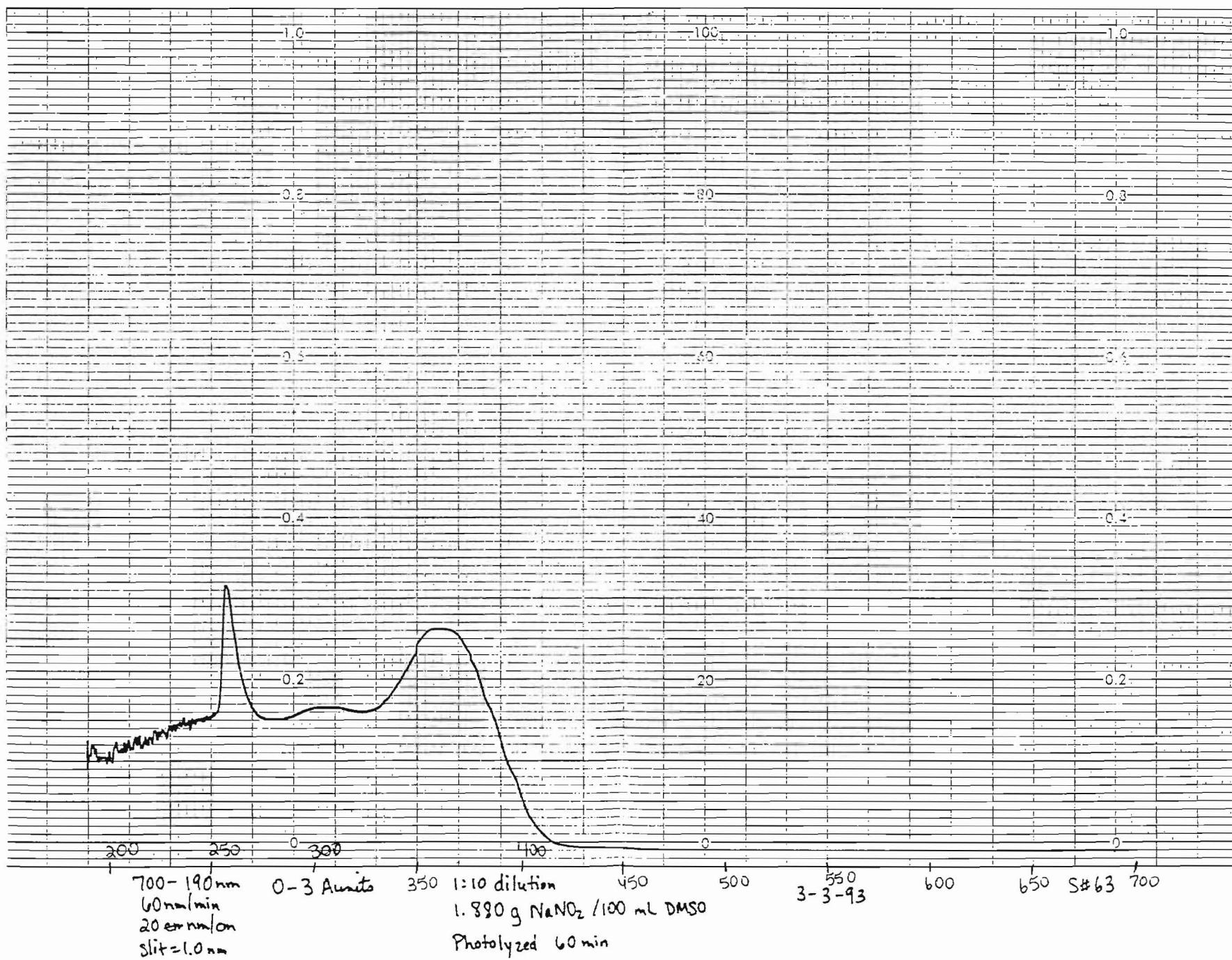
S# 78

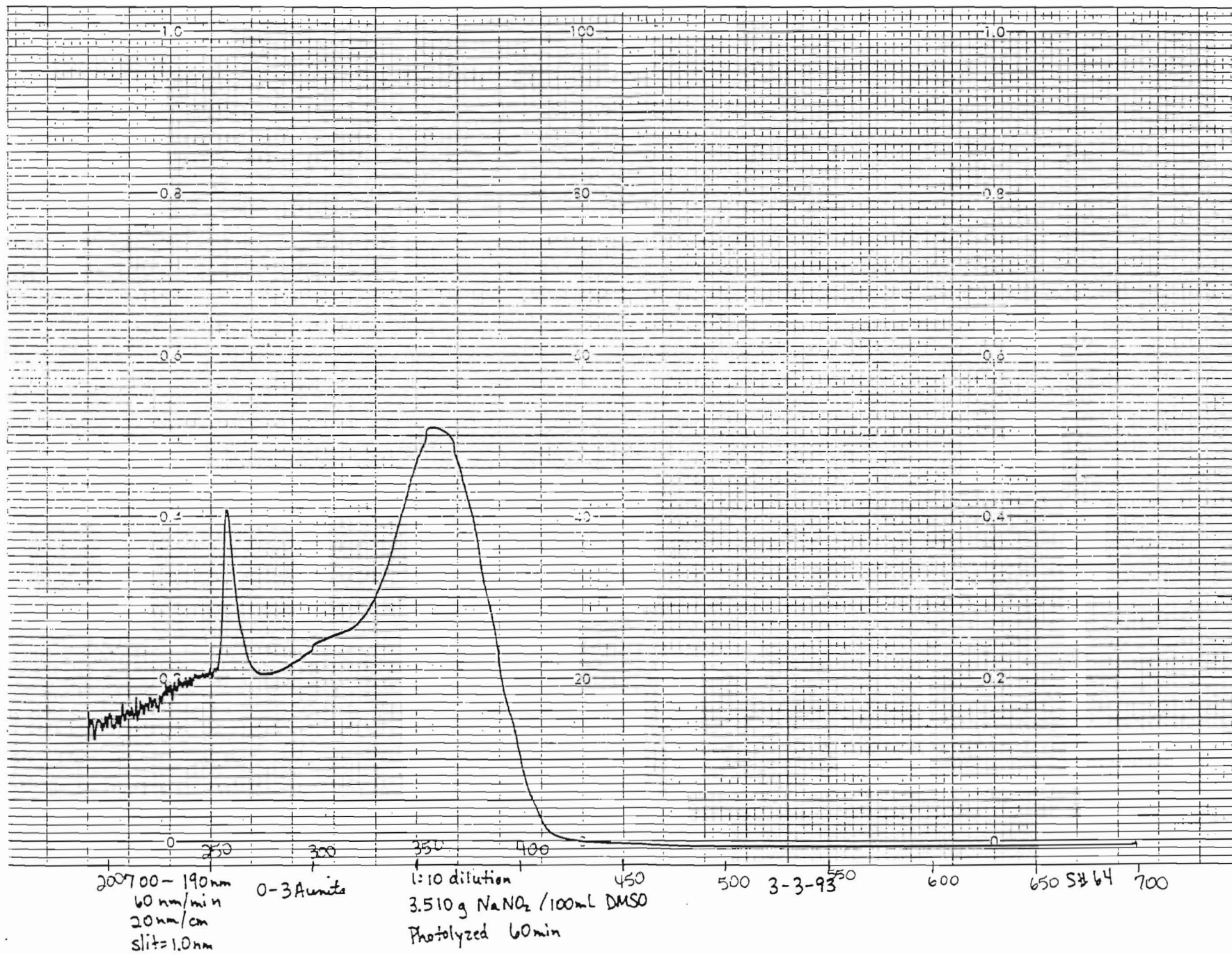
A56



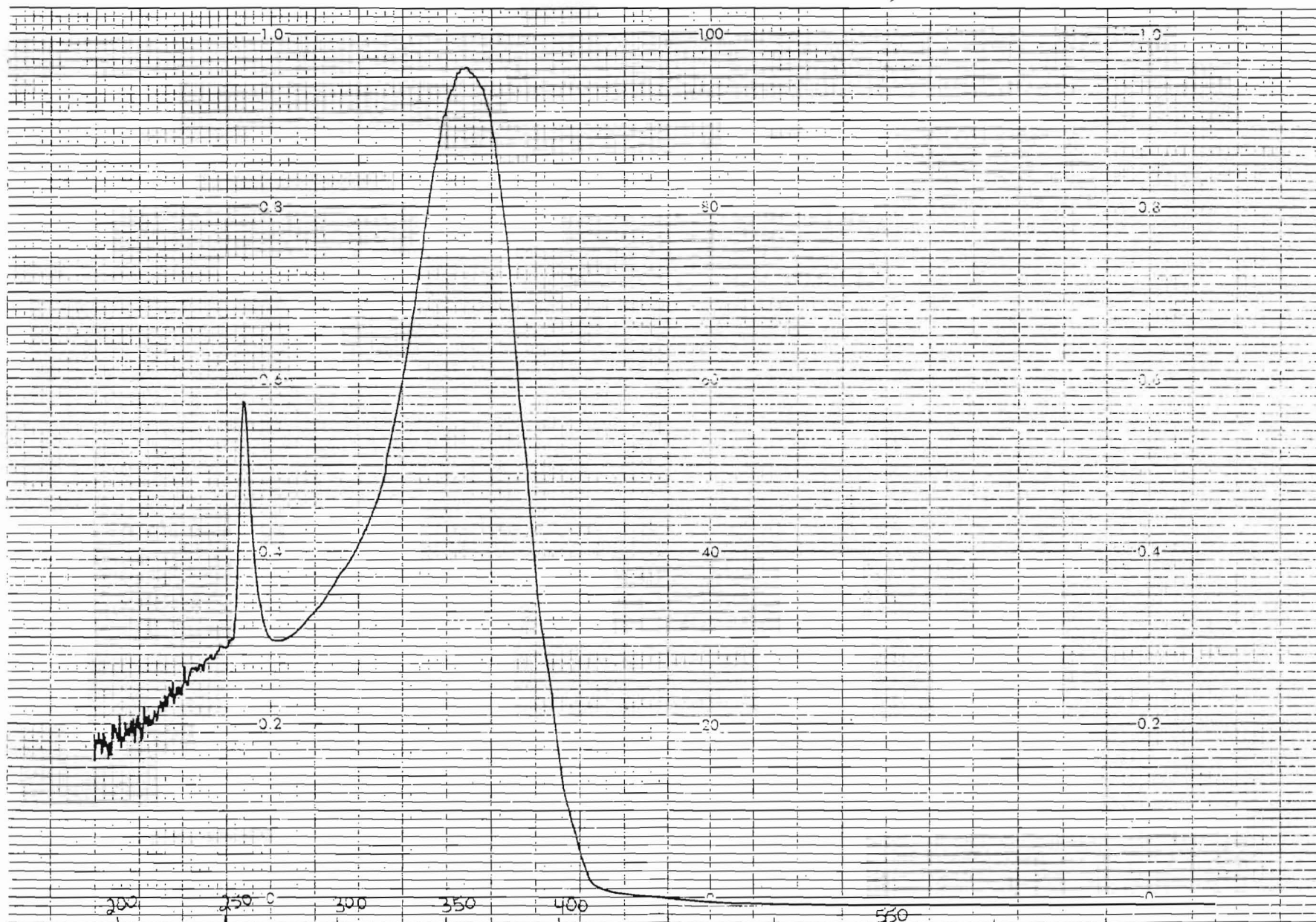








A60



700-190 nm  
60 nm/min  
20 nm/cm  
Slit = 1.0 nm

0-3 Abs units

1:10 dilution  
6.919 g  $\text{NaNO}_2$  / 100 mL DMSO  
Photolyzed 60 min

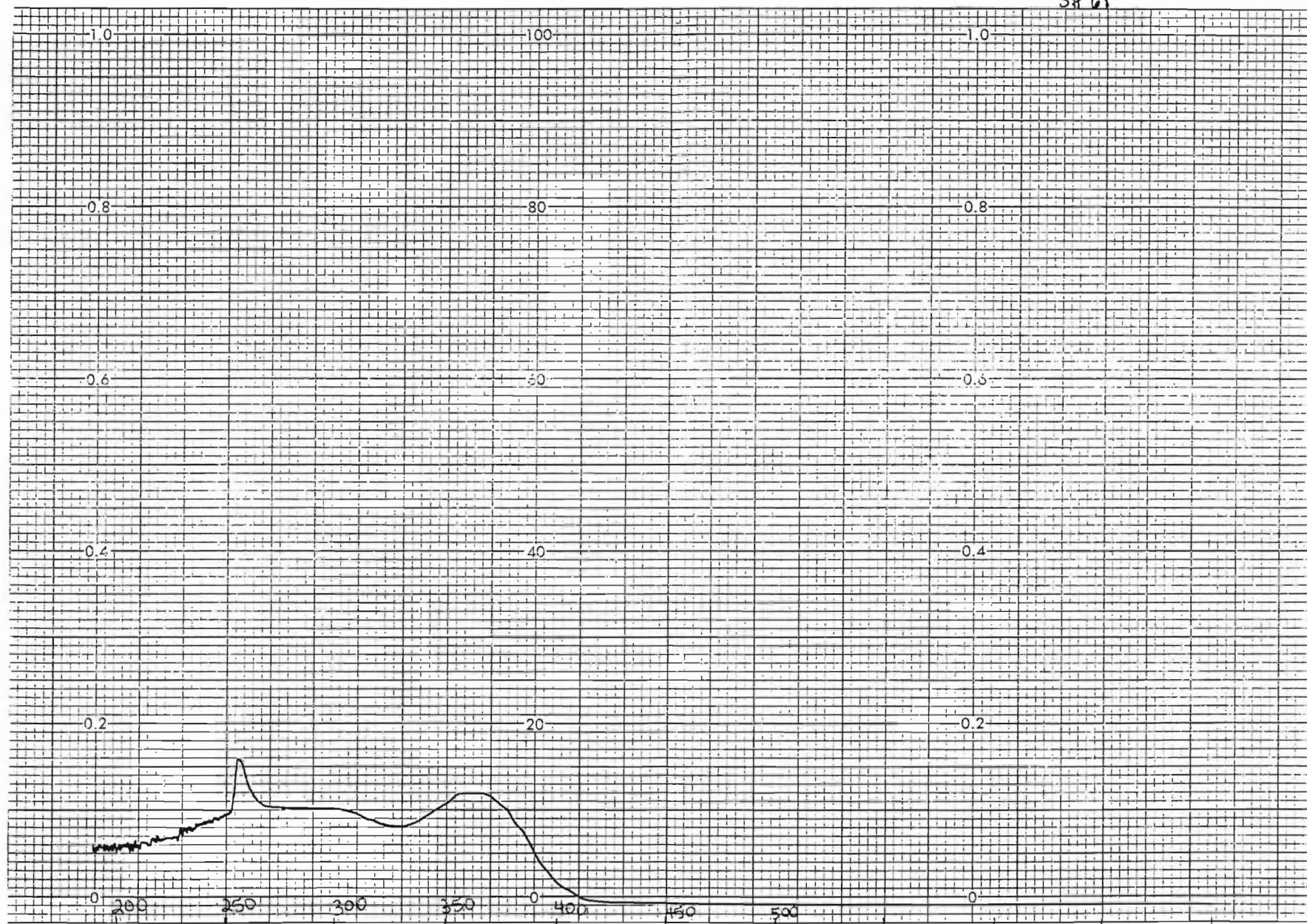
3-3-93

650 S# 65 700



A61

S# 68

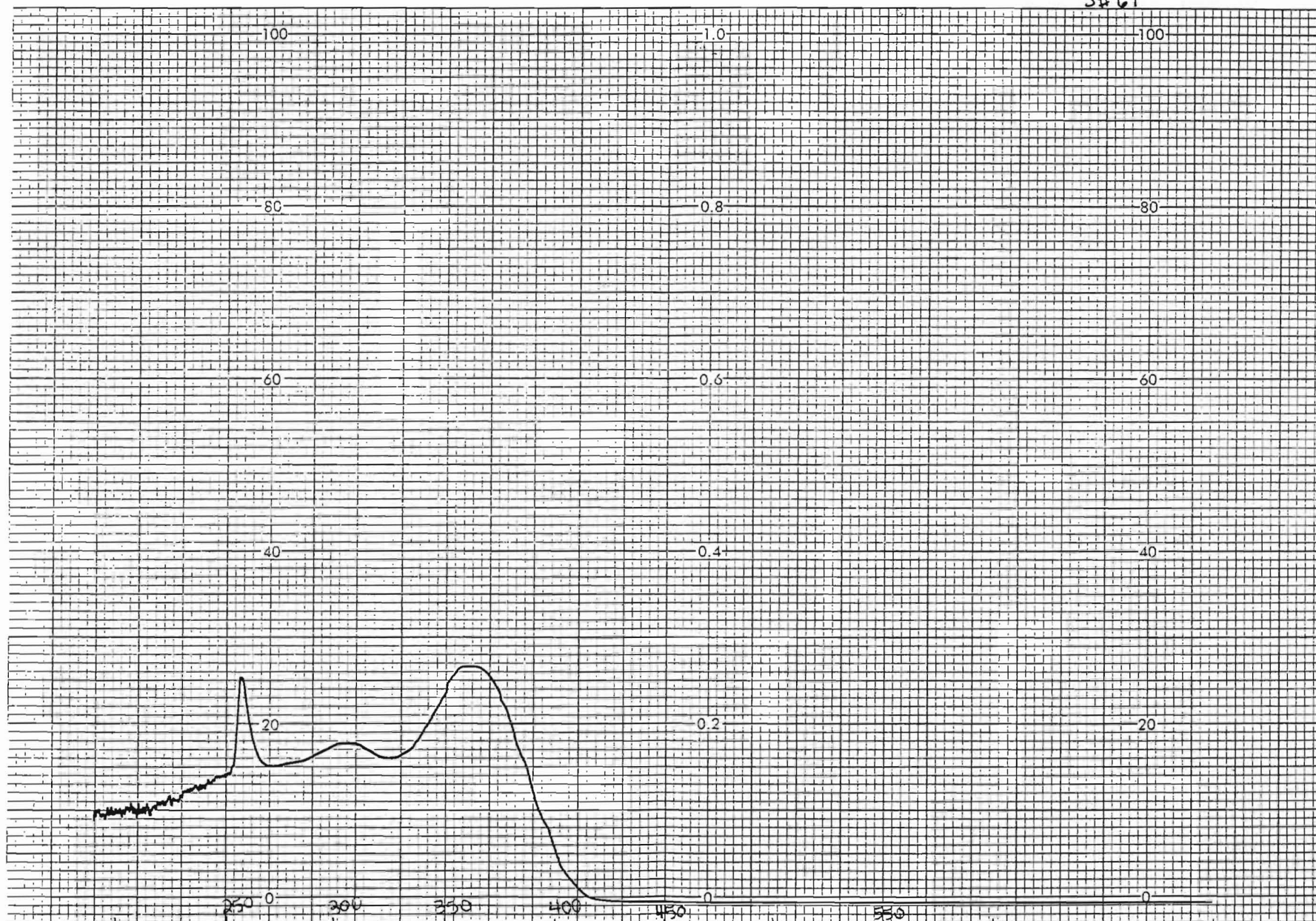


700-190 nm  
60 nm/min  
20 nm/cm  
Slit = 1.0 nm  
0-3 A units

0.886 g NaNO<sub>2</sub> / 100 mL DMSO  
2<sup>nd</sup> photolysis 60 min  
1:10 dilution

3-17-93 550 600 650 700

S#69



200-190 nm  
60 nm/min  
20 nm/cm  
slit=1.0 nm

0-3 Aunits

1.880 g  $\text{NaNO}_2$  / 100 mL DMSO  
2<sup>nd</sup> Photolysis 60 min  
1:10 dilution

3-17-93

600

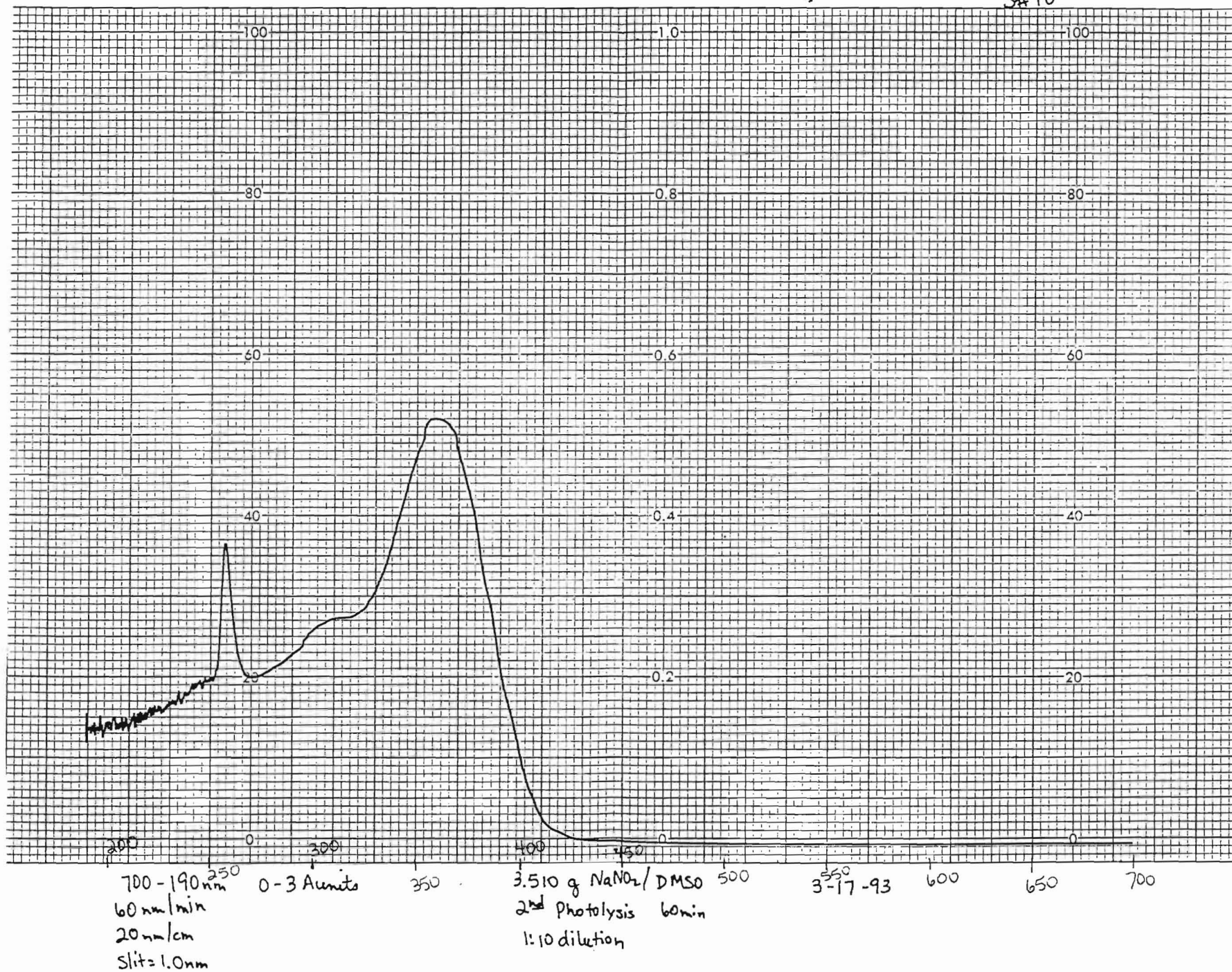
650

700

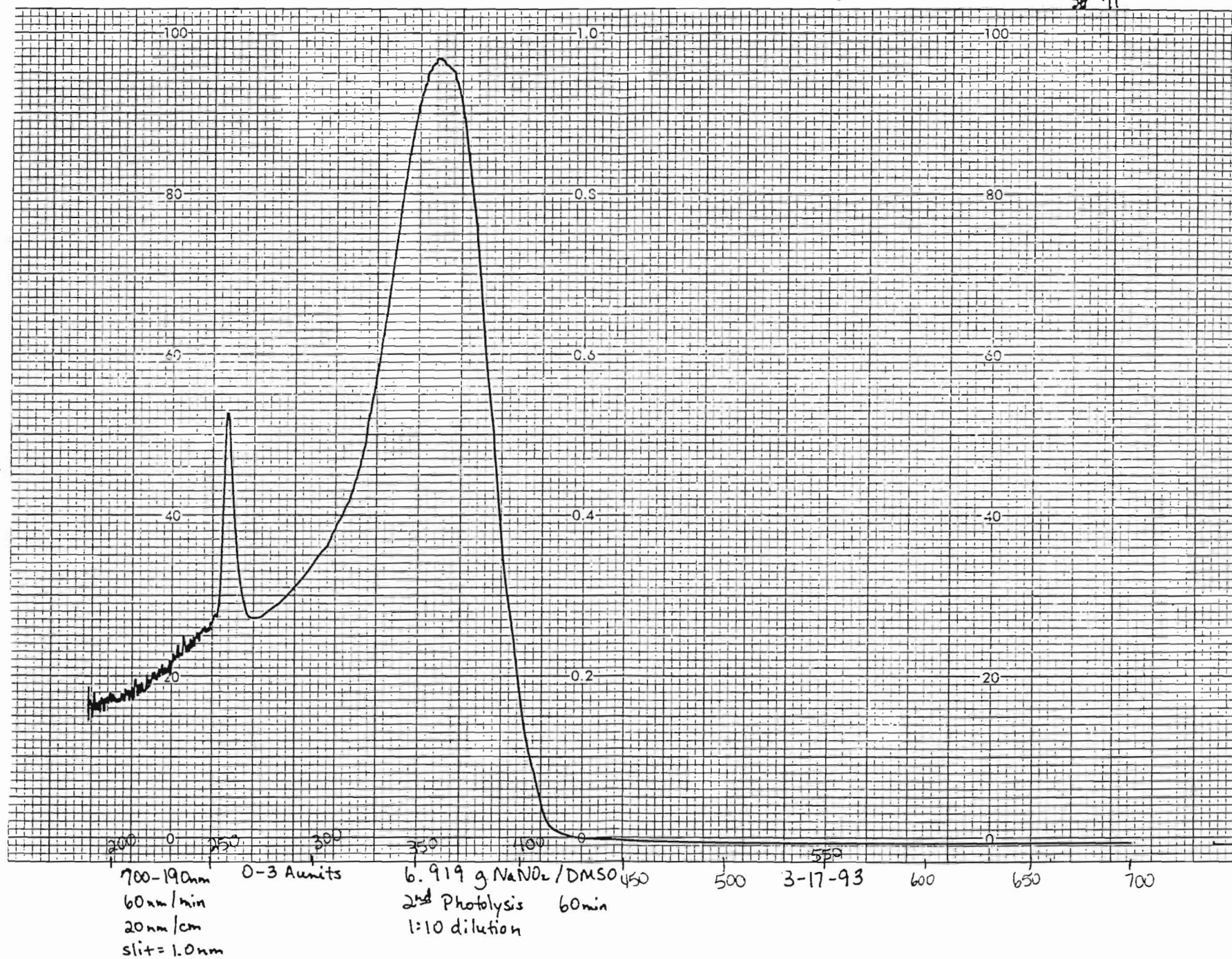


A63

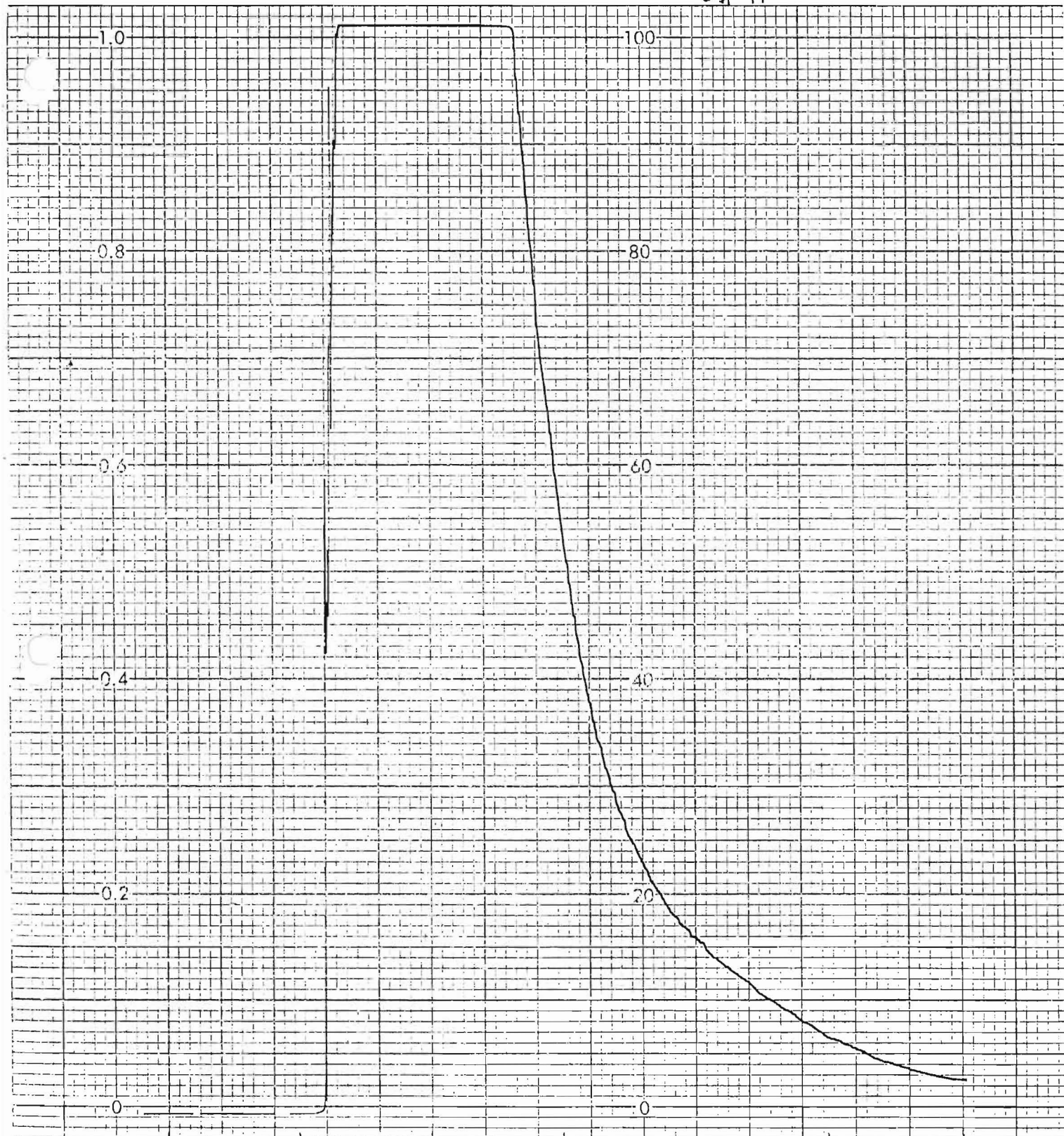
S#10







S# 41



500-190 nm  
60 nm/min  
20 cm/min  
slit = 1.0 nm

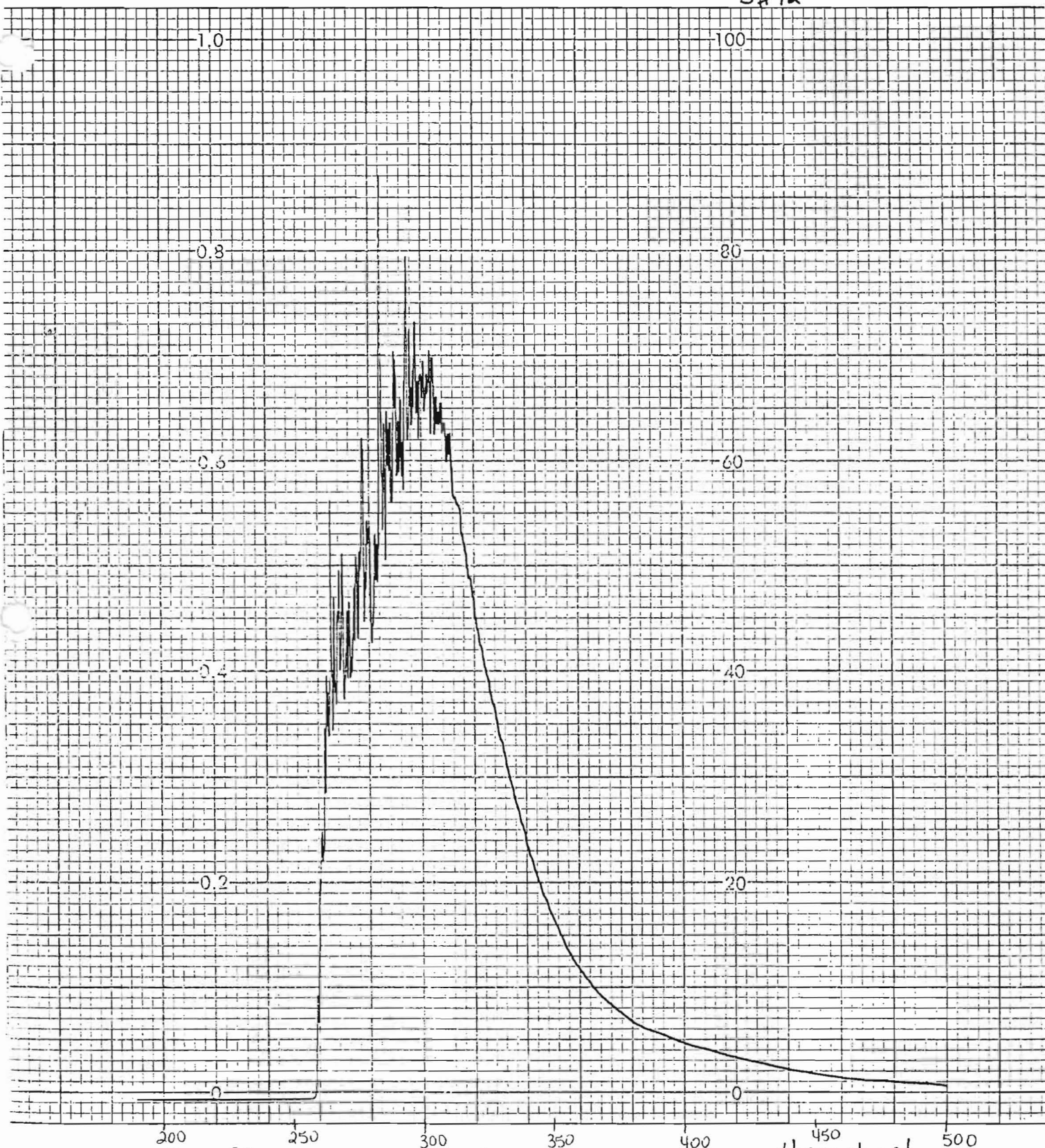
0-1 A unit

11-24-92

thermolyzed DMSO  
vs. non-thermolyzed  
DMSO



S#42



500-190nm  
60 nm/min  
20 cm/min  
Slit=1.0nm

0-3 Aunit

11-24-92

thermolyzed  
DMSO

SH43



500-190 nm  
60 nm/min  
20 ~~nm~~ /min  
slit = 1.0 nm

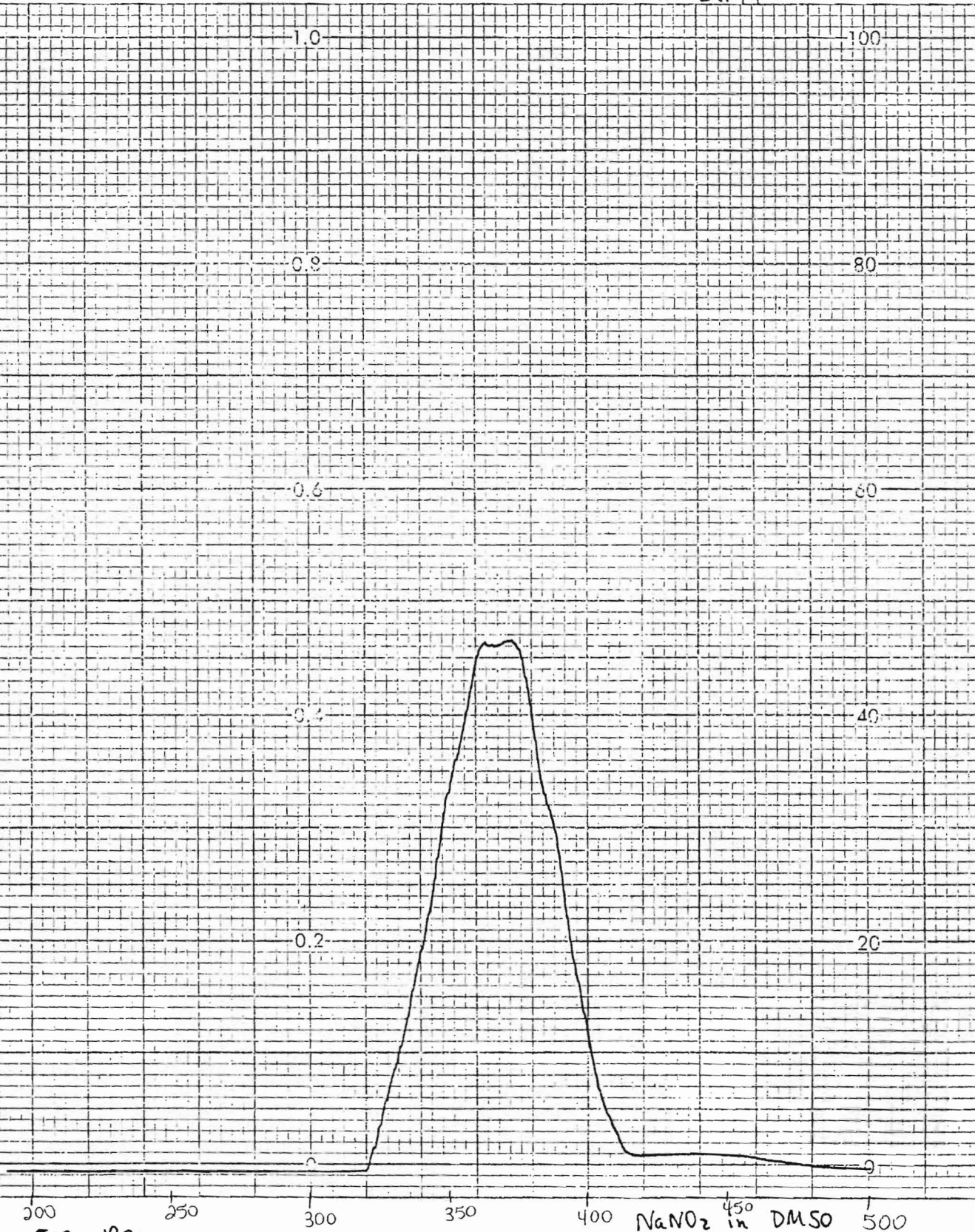
0-3 A unit

11-24-92

NaNO<sub>2</sub> in DMSO  
thermolyzed



SA44



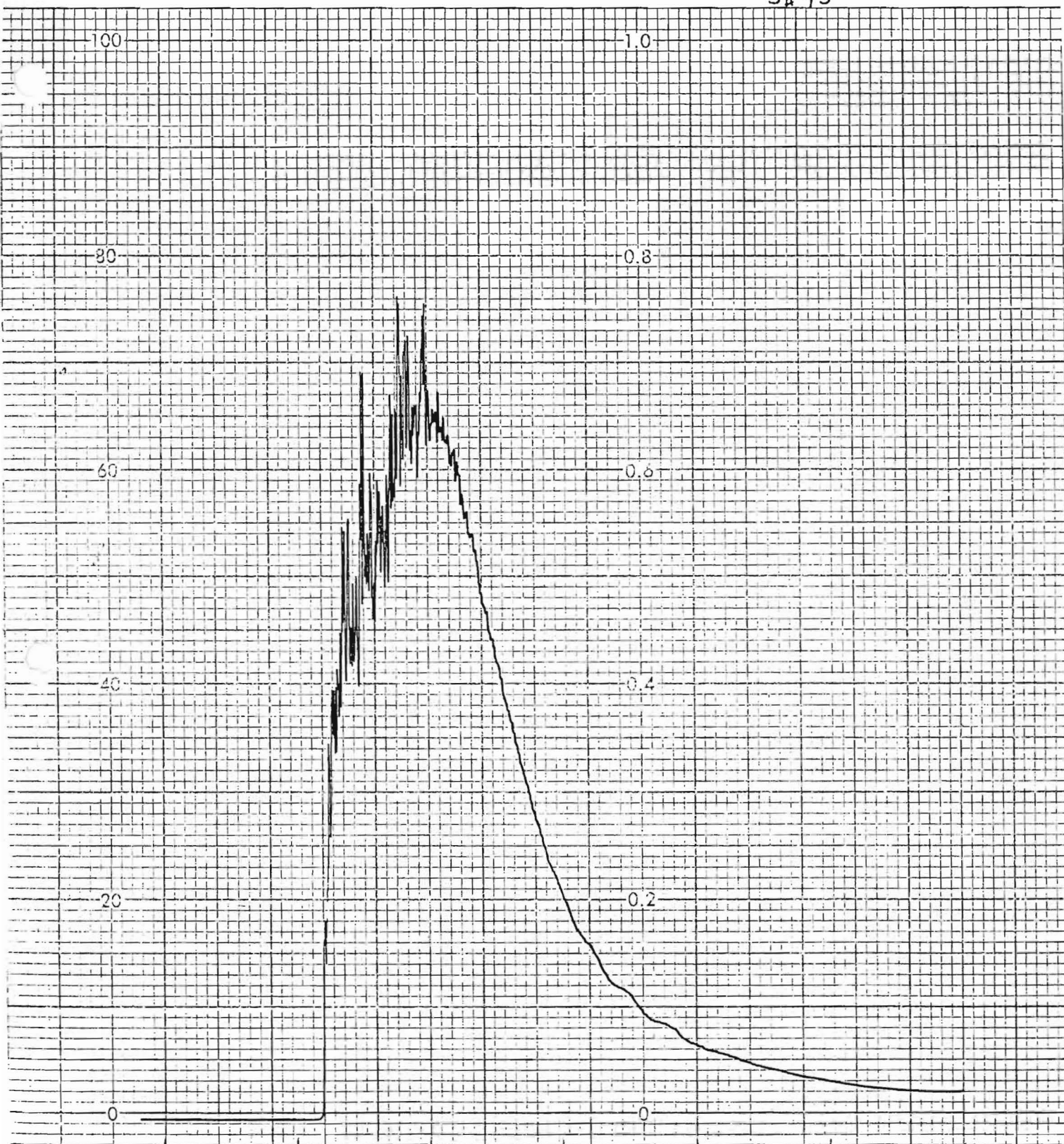
500 - 190 nm  
60 nm/min  
20 cm/min  
Slit = 1.0 nm

0 - 1 Aunit

11-24-92

NaNO<sub>2</sub> in DMSO  
thermolyzed

S#45



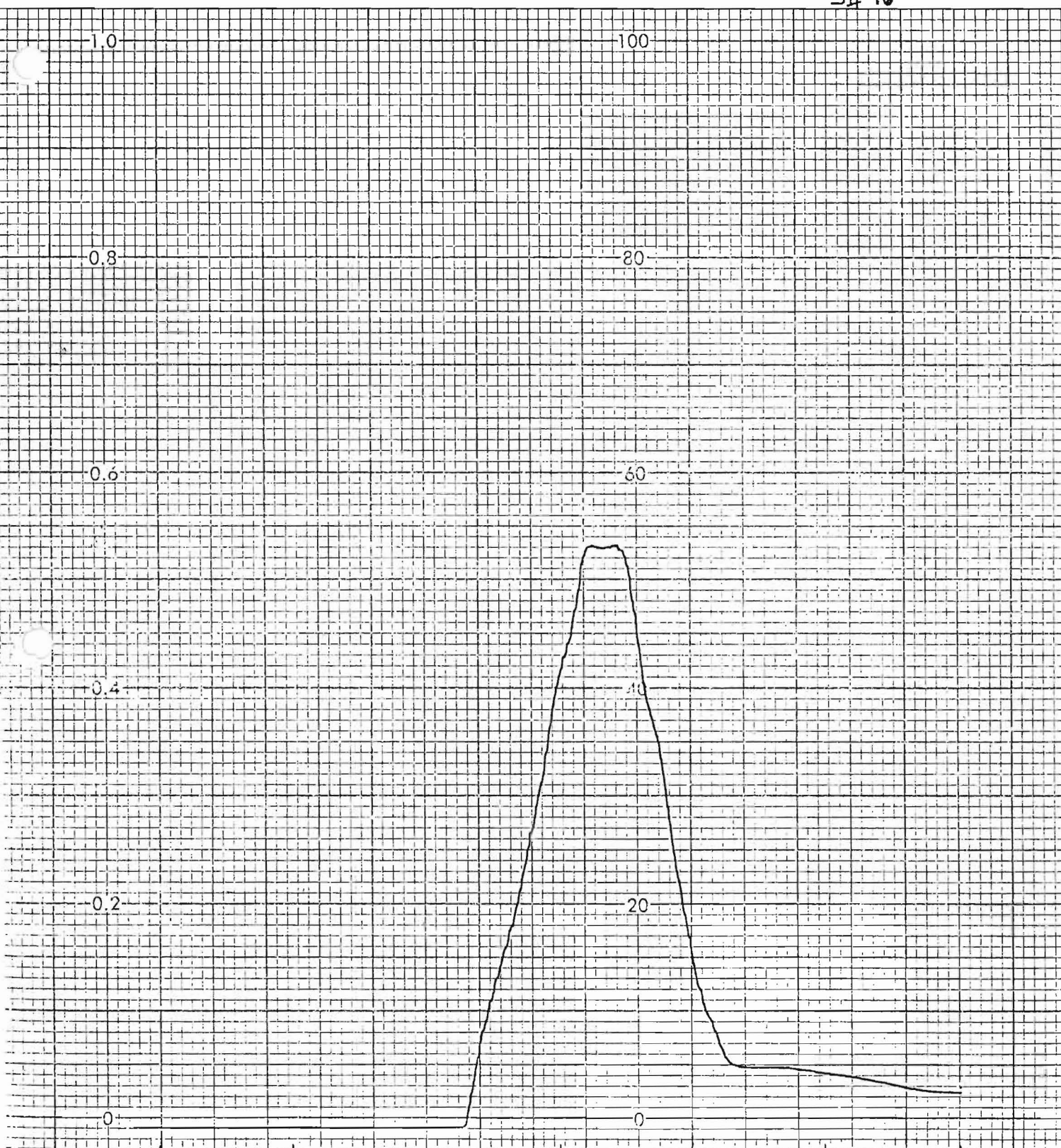
500 - 190 nm  
60 nm/min  
20 Bm/min  
slit = 1.0 nm

O-3 Aunit 11-24-92

thermo lyzed  
DMSO  
bubbled with  
N<sub>2</sub>



S# 46



200 250  
500 - 190 nm

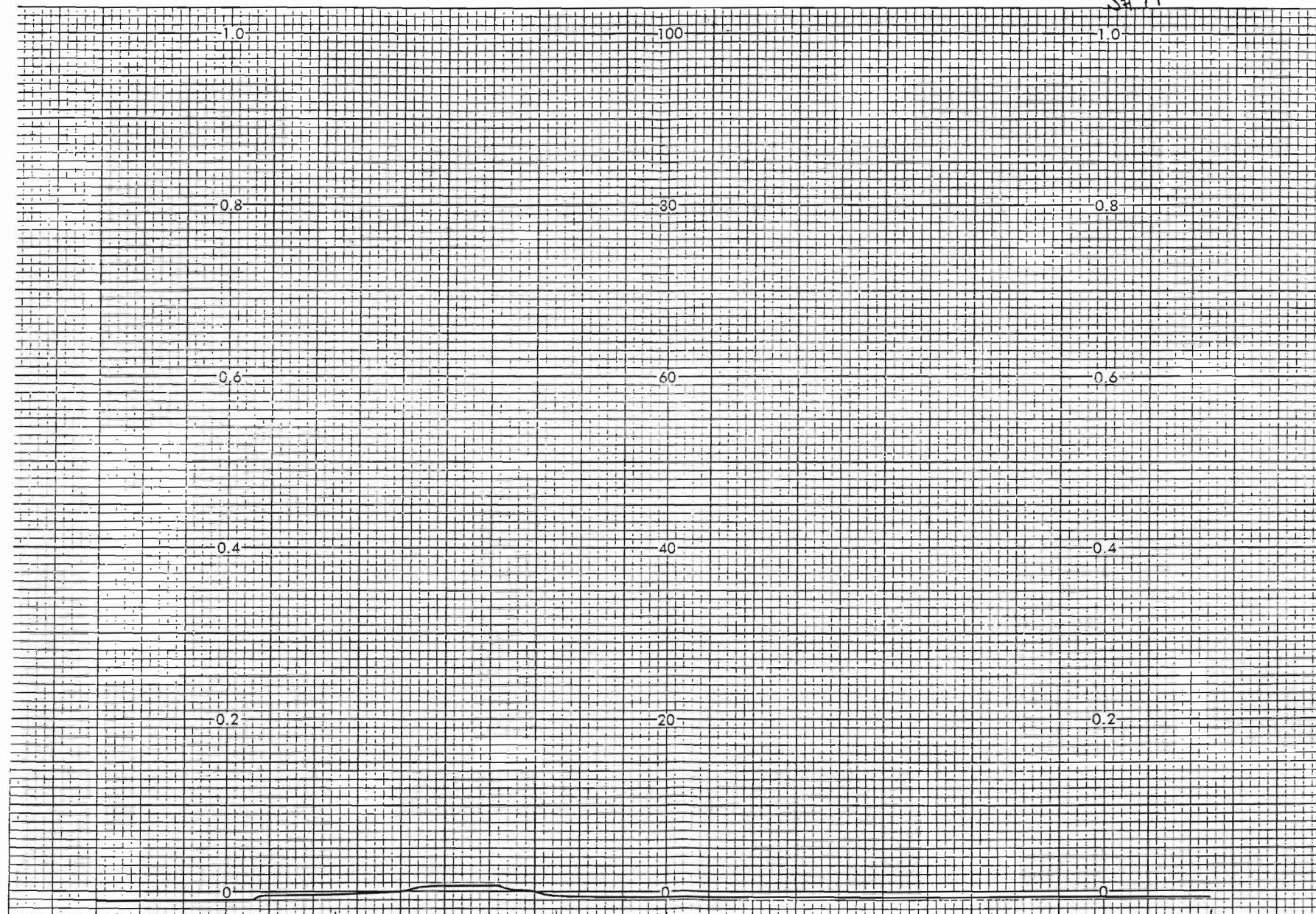
60 nm/min  
20 cm/min  
slit = 1.0 nm

0 - 1 A unit

11-24-92

NaNO<sub>2</sub> in  
DMSO  
thermolyzed  
bubbled with  
N<sub>2</sub>

S#79

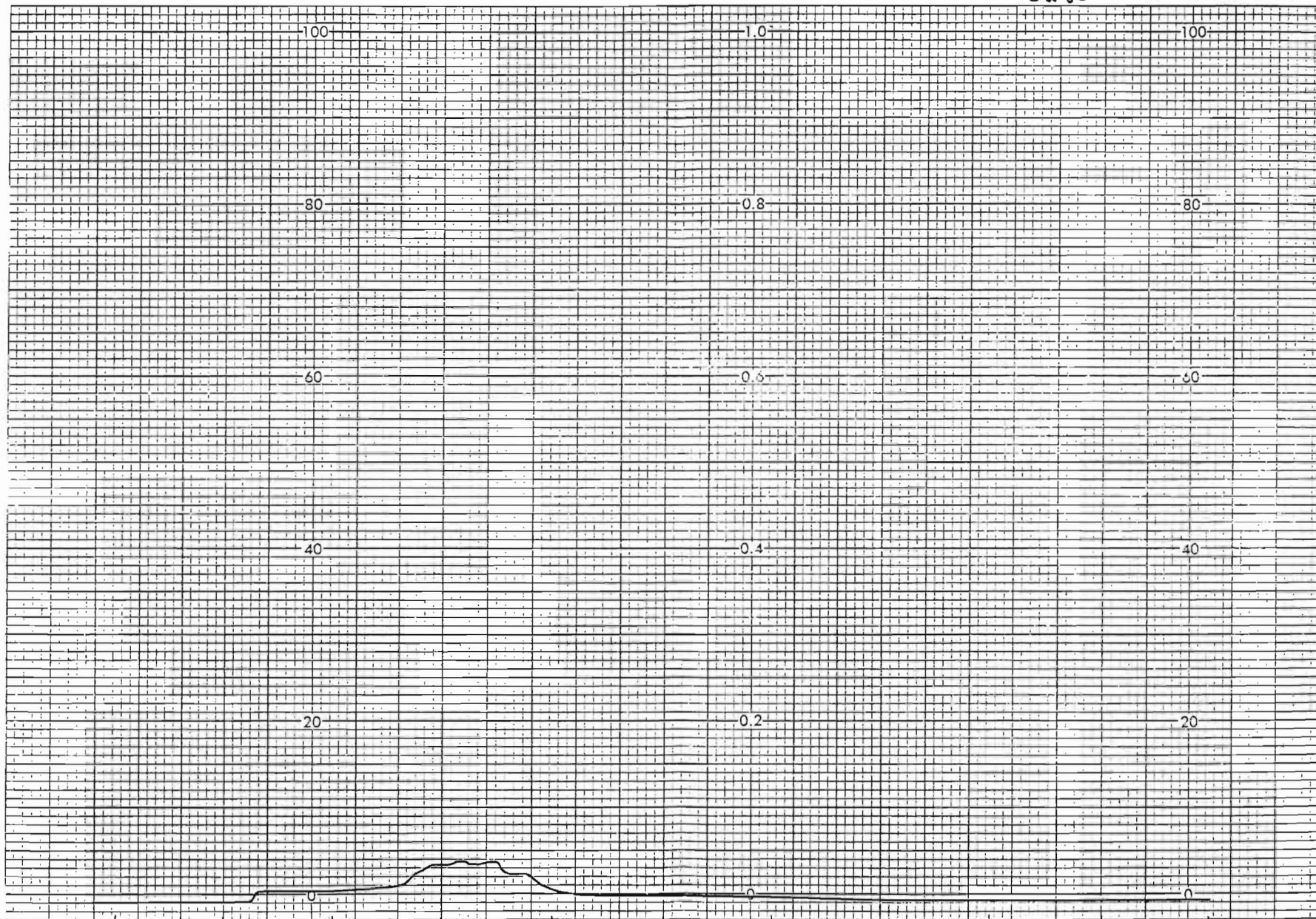


200 700-190 nm 250 0-3 A units 300  
 60 nm/min  
 20 nm/cm  
 slit=1.0mm  
 thermolyzed DMSO  
 in N<sub>2</sub>  
 60 min at 60°C  
 vs. DMSO  
 4-7-93 600 650 700

A71



S#80



200-190 nm  
60 nm/min  
20 nm/cm  
Slit = 1.0 nm

D-1 A unit

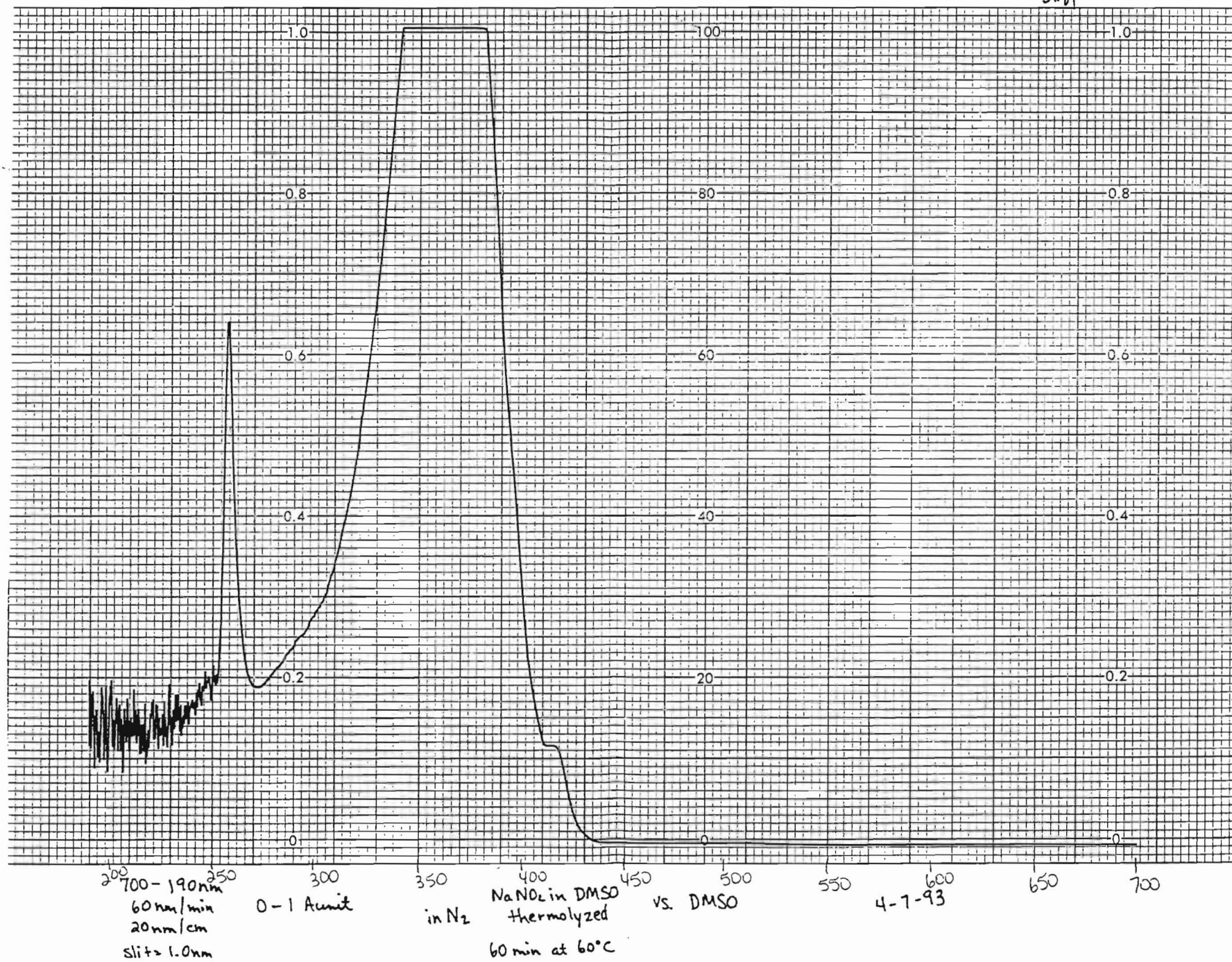
thermolyzed DMSO  
in N<sub>2</sub>

vs. DMSO

4-7-93

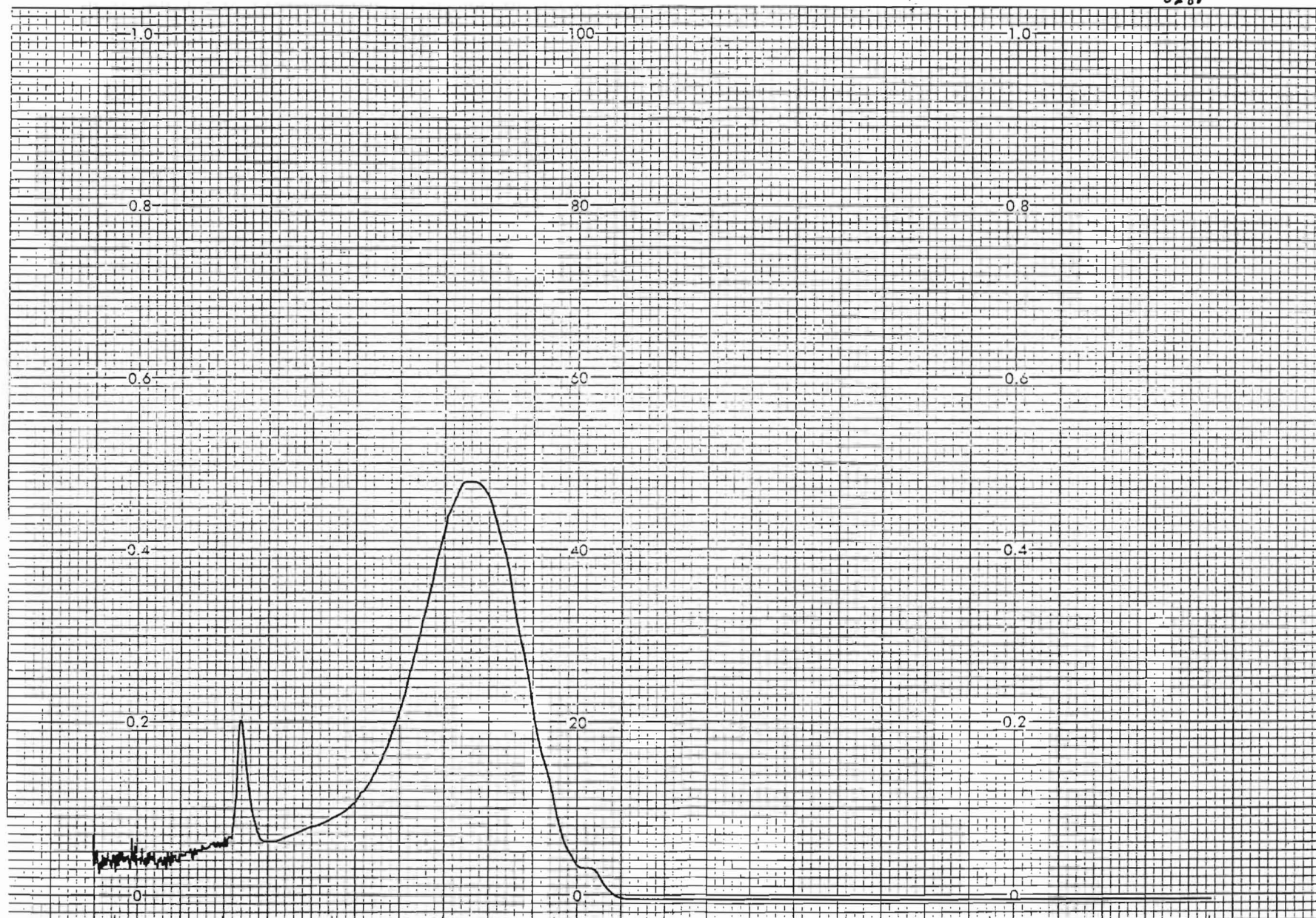
60 min at 60°C

S#81





588.



200 - 190 nm

60 nm/min

20 nm/cm

Slit = 1.0 nm

0 - 3 A units

300

350

1:10 Dilution

400

450

500

550  
4-7-93

600

650

700

in N<sub>2</sub>

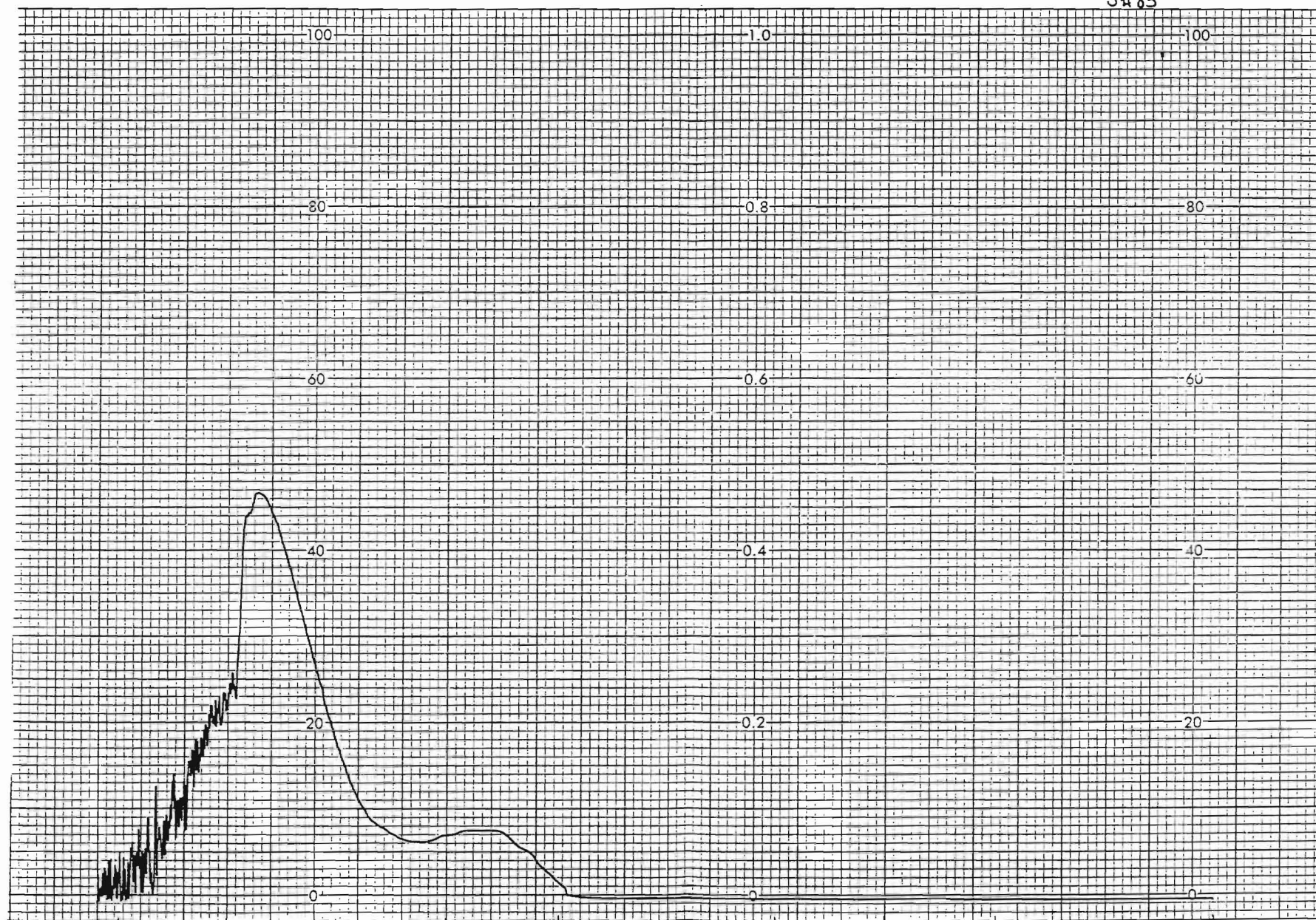
NaNO<sub>2</sub> in DMSO  
thermolyzed

vs. DMSO

60 min at 60°C



S#83



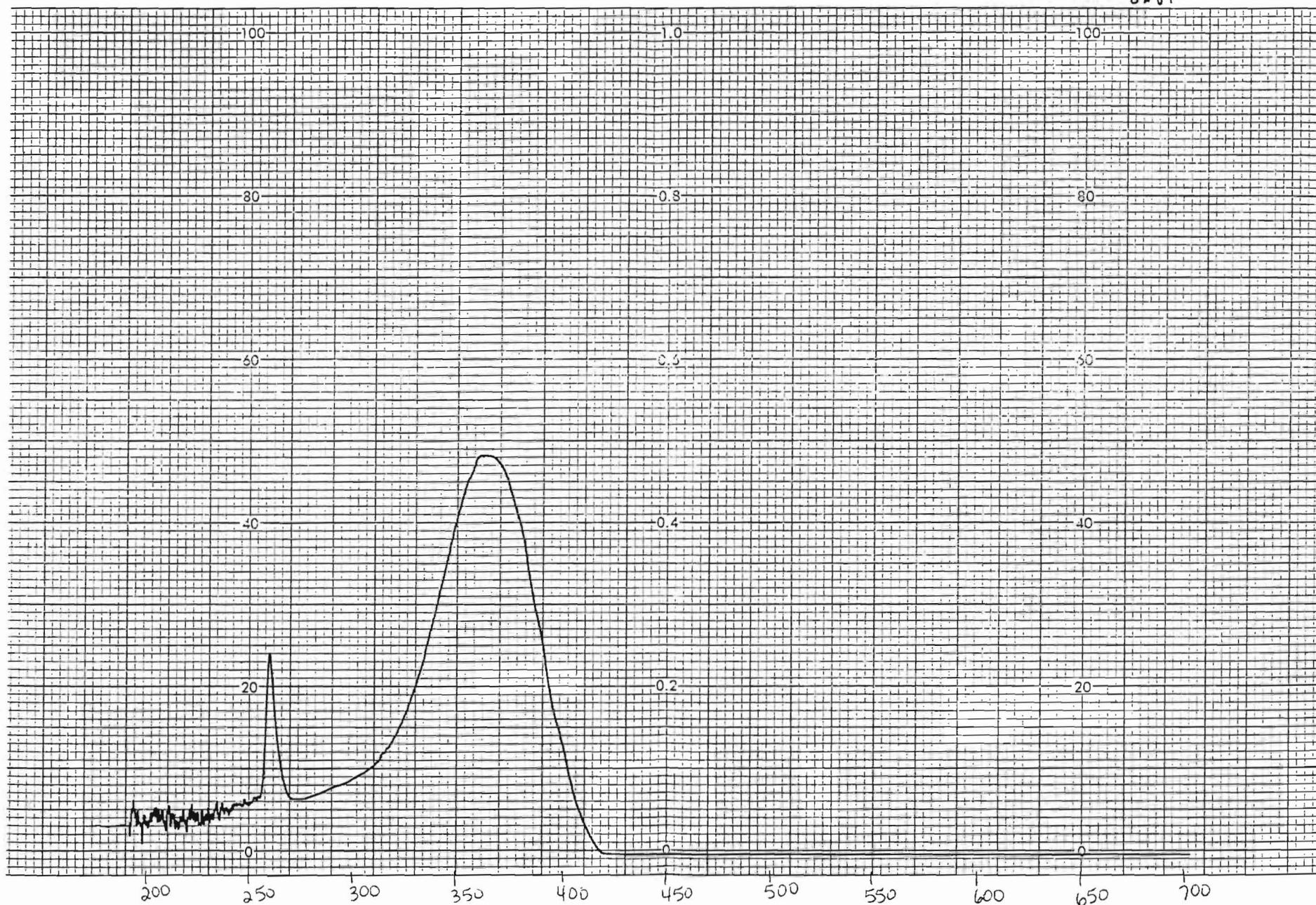
200-190nm  
60 nm/min  
20 nm/cm  
slit = 1.0nm

O-1 A unit

DMSO  
in O<sub>2</sub>  
thermolized  
60 min at 60°C  
vs. DMSO

4-7-93

S#84



1:10 dilution

NaNO<sub>2</sub> in DMSO  
thermolyzed

vs. DMSO

0-3 A unit

700-190nm  
60nm/min  
20nm/cm

slit = 1.0nm