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THE STUDY OF THE SYNTHESIS OF GLYCEROL

12 February 1970 - 15 November 1970
ANNUAL REPORT

Prepared under Contract No NAS2-4496

for

National Aeronautics and Space Administration
Ames Research Center Moffett Field, California 94035

GR-10-SSG-70

ESSO RESEARCH AND ENGINEERING COMPANY

Government Research Laboratory

Linden, New Jersey

N71-17676
(ACCESSION NUMBER)
186
(PAGES)
CR-114276
(NASA CR OR TMX OR AD NUMBER)
63
(THRU)
06
(CATEGORY)
FACILITY FORM 602

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NASA STI FACILITY
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STUDY OF SYNTHESIS OF GLYCEROL

by

C M Kouidri and W F Taylor

November 15, 1970

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Prepared Under Contract NAS2-4496

by

ESSO RESEARCH AND ENGINEERING COMPANY
GOVERNMENT RESEARCH LABORATORY
LINDEN, N J

for

DR JACOB SHAPIRA, TECHNICAL MONITOR
ENVIRONMENTAL CONTROL RESEARCH BRANCH
AMES RESEARCH CENTER
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

GR-10-SSG-70

Esso Project No 4320
Annual Report
12 February 1970 - 15 November 1970

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FOREWORD

This report was prepared by the Government Research Laboratory, Esso Research and Engineering under Contract NAS2-4496 This program is monitored by Dr Jacob Shapira, Environmental Control Research Branch, National Aeronautics and Space Administration, Ames Research Center

This report covers work conducted from February 12, 1970 to November 15, 1970. Dr Cherif M Kouidri and Dr. William F Taylor were the key personnel on the program assisted by Mr Ronald M Buono. The program was administered by Dr Daniel Grafstein

I INTRODUCTION

Two of the most pressing problems of life support in space are food supply and waste gas disposal The possibility of converting waste gases (CO_2, H_2O) into foodstuffs to be used during extended spaceflight has interested NASA for sometime A study (1) which surveyed and critically evaluated methods for the production of fatty acids and lipids from metabolic wasted concluded that the only promising route was the one leading to glycerides The method involved synthesis of ethylene from carbon monoxide, polymerization to α-olefins via the Ziegler growth reaction, conversion to fatty acids by oxidative ozonolysis and esterification with glycerol to form glycerides However, from an engineering standpoint, the synthesis appeared to be too complex to be seriously considered on board a spacecraft

The nutritional value of glycerol, which has been proposed by many workers as a promising source of metabolic energy (calories) on board a spacecraft (1,2,3) has been established (3,4,5). It has been fed at levels up to 41% with no deleterious effects and has been shown to act as a source of dietary energy (4). Also, glycerol was thought to be easier to synthesize than the more complicated compounds such as fatty acids and lipids Another source of metabolic energy is propylene glycol Feeding studies revealed that the latter was even less toxic than glycerol when injected in dilute form (6) Intramuscularly and subcutaneously a minimum fatal dose (for rats) of propylene glycol was found to be 15 7 and 23 1 g per kg of animal weight, respectively, as compared to corresponding values of 7 5 and 15 1 g

per kg, respectively, for glycerol These results are in agreement with the observations made earlier by Seidenfeld and Hanzlik (7) and later with the findings of Morris, et al (8) In all investigations on propylene glycol, the latter authors observed no noticeable effects of deleterious nature except in cases where large acute doses were administered The absence of any significant weight loss at the highest dosage and the satisfactory growth observed (6) at the lower dosages indicate that 4 to 8 cc of propylene glycol per Kg of animal weight are tolerated by rabbits for a period of 50 days without any toxic symptoms other than slight anorexia The low toxicity of propylene glycol (compared to glycerol) recommends it as a potential nutrient

In response to RFP A13053(HK-34), Esso Research and Engineering Company proposed (9) The Study of the Synthesis of Glycerol, Contract NAS2-4496

Using formaldehyde as the starting material, two routes were available, the first leading to glycerol, the second to a mixture of glycerol and porpylene glycol

a) Selective trimerization of formaldehyde to glyceraldehyde and dihydroxyacetone followed by hydrogenation to yield glycerol.

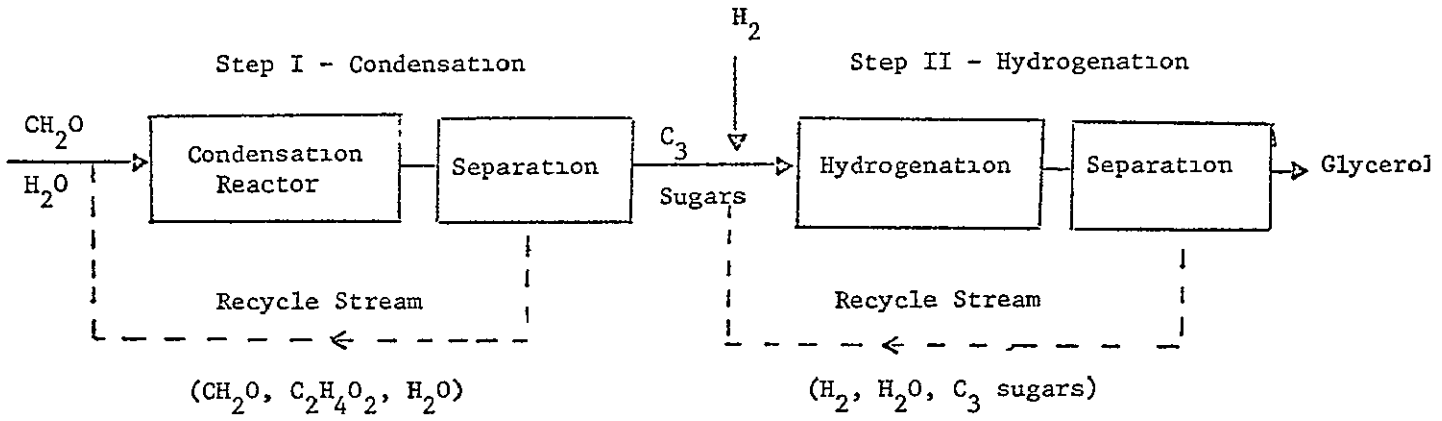
b) controlled condensation of formaldehyde to hexoses followed by catalytic reduction cleavage to glycerol and propylene glycol.

The first major goal of this study was to select the more promising route for the continuous production of 5 kg/day of "pure" (CP) glycerol After examining the merits of competing routes, the formaldehyde trimerization route was chosen initially and the majore emphasis of the early laboratory work was on the chemistry of the system, including a definition of a number of parameters of the system such as kinetics, heterogeneous and homogeneous catalysts and other basic variables of the system

Early results (Final Report 1968) suggested that the formaldehyde trimerization reaction could be kinetically controlled so that its product mixture would largely consist of C_3 sugars which, upon mild hydrogenation, would yield the desired product, i e , glycerol Unreacted formaldehyde and glycolaldehyde were to be recycled in a process as shown in Figure 1 Subsequently, additional experimental work (Final Report 1969) on the dimerization and trimerization of glycolaldehyde showed that these two reactions as well as that of C_2 with C_3 carbohydrate to form C_5 sugars were too fast to allow reasonable yields of low carbon number carbohydrates (glyceraldehyde and dihydroxyacetone) to accumulate at useful conversion levels This, coupled with the lack of a good sugar fractionation method which would allow unconverted glycolaldehyde to be recycled compelled us to alter the approach

Figure 1

Schematic of Process for the Production of Glycerol



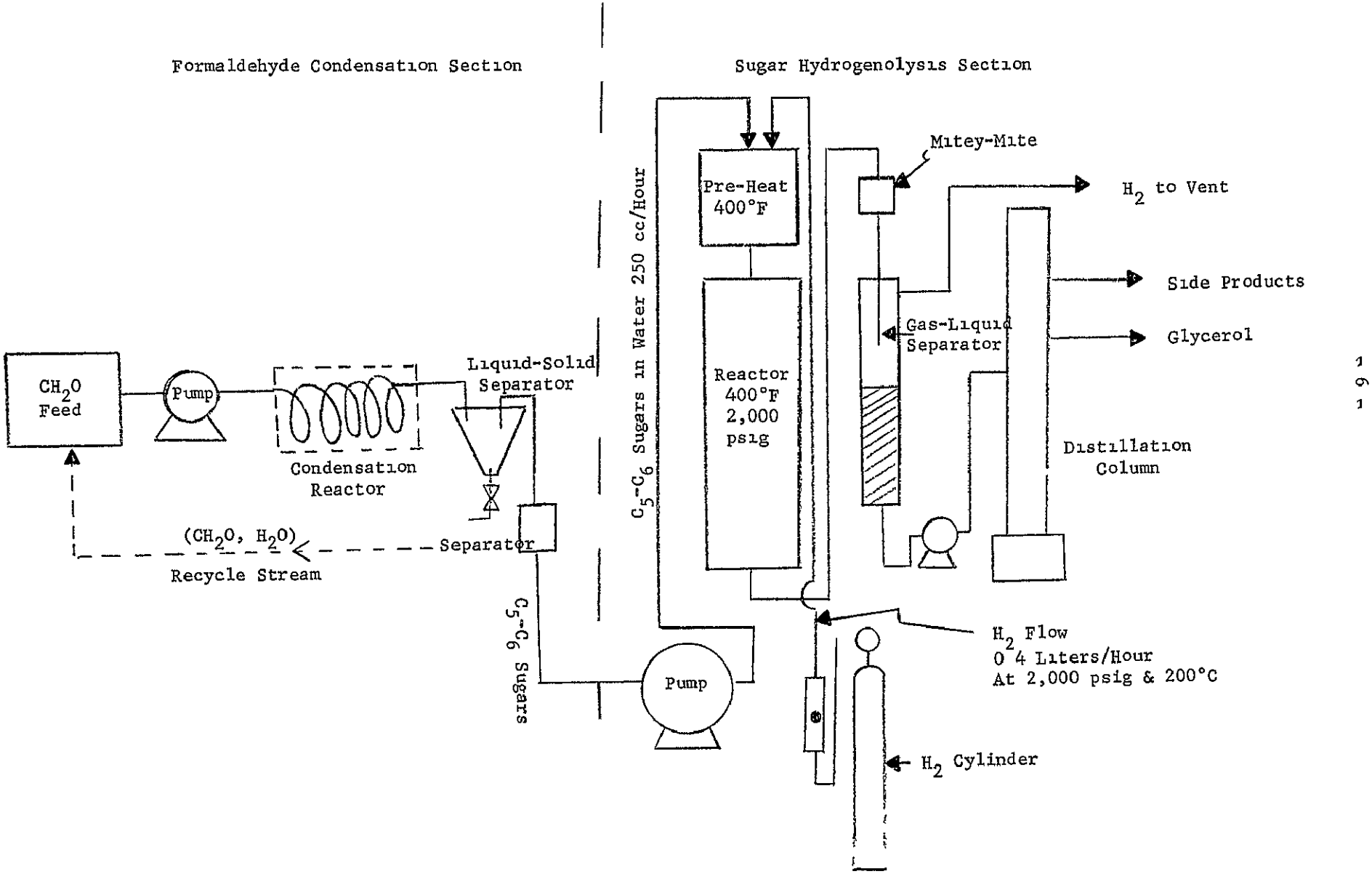
Under the current program, the effort was redirected to the second route, allowing the formaldehyde condensation reaction to proceed to the C_5-C_6 carbohydrate stage followed by reductive cleavage of the latter mixture to an edible product, namely glycerol and propylene glycol. That high carbon number carbohydrates undergo catalytic reductive cleavage to yield glycerol and/or propylene glycol has been shown by several authors (10-15). These published studies employed neat sugars as starting materials and were unanimous in pointing out the sensitivity of the reaction towards experimental conditions

Thus, under the present program, the two-step approach to edible polyol synthesis was tested and its feasibility demonstrated. Studies of experimental conditions (residence time, catalyst to co-catalyst concentration) under which the formose reaction would yield the largest quantities of pentoses and hexoses were conducted Also, conditions under which neat C_5-C_6 sugars can be hydrogenolyzed to afford (catalyst type, temperature, hydrogen pressure, carbohydrate structure) reasonable yields of edible polyols (i e , glycerol and propylene glycol) were studied Such conditions were employed for the hydrogenolysis of formose mixtures generated under different residence times so that the latter variable affecting C_5-C_6 carbohydrates could be optimized. Glycerol was obtained from formaldehyde for the first time and its separation from the hydrogenolysis product mixture was investigated

Finally, a breadboard glycerol synthesis unit based on this two-step approach (controlled condensation of formaldehyde to C_5-C_6 sugars followed by reductive cleavage) was designed (Figure 2), constructed and operated This report describes and discusses the results obtained on all aspects of the program

Figure 2

Edible Polyol Synthesis Unit



II. SUMMARY OF CURRENT PROGRAM'S ACHIEVEMENTS

The approach to edible polyol synthesis which is based on driving the formaldehyde condensation reaction to the C_5-C_6 carbohydrate stage followed by reductive cleavage to glycerol and propylene glycol was shown to be feasible, for the first time both edible polyols were produced directly from formaldehyde.

Studies of the complex formose synthesis revealed that the reaction can be controlled to produce maximum yields of C_5-C_6 sugars The latter were found to be highest at the moment of complete or near complete entering formaldehyde conversion However, when reaction time exceeds that required for complete formaldehyde conversion, other alkali-promoted reactions begin to occur and as a result, pentose and hexose content diminishes This was confirmed by studies in which formose mixtures generated under varying residence times were hydrogenolyzed under the best reductive cleavage reaction conditions The formose mixture which contained the larger quantity of pentose and hexose material yielded, upon hydrogenolysis, 22 08% C_3 polyols The poorer mixture, obtained under the longest residence time, afforded only 5 77% C_3 polyols

Conditions for the hydrogenolysis reaction of formose mixtures were obtained as a result of an extensive study of the catalytic reductive cleavage reaction of neat carbohydrates This study included investigation

of the effects of catalyst type, carbohydrate structure, and hydrogen pressure on total C_3 polyol yield The results showed that, while ruthenium on carbon used in conjunction with $Ca(OH)_2$ produced the largest quantities of edible polyols, it also promoted the hydrogenation of the pentose and hexose materials In fact, production of C_5-C_6 polyols was always larger than edible triol formation regardless of the nature of the starting material (i e , neat carbohydrate or formose mixture) Selectivity of the hydrogenolysis system to glycerol and propylene glycol must be improved in order to make the two-step process practical. This can be achieved by designing and fabricating catalysts which will a) promote complete reduction of C_5-C_6 sugars to their corresponding polyols followed by cracking to glycerol or propylene glycol or b) cleave the starting material selectively to C_3 fragments followed by hydrogenation to the desirable edible polyols

Separation via fractional distillation of glycerol from the hydrogenolysis product mixture was attempted Glycerol was successfully separated from other components of the mixture Unfortunately, the presence in the still of materials which decomposed very near glycerol's distillation temperature prevented the collection of a pure sample The problem of separating the edible propylene glycol from inedible ethylene glycol remains to be tackled

III OVERVIEW OF THE PROGRAM

Analysis of all data obtained on the Study of the Synthesis of Glycerol leads us to make the following conclusions and recommendations Selective trimerization of formaldehyde to glyceraldehyde and dihydroxyacetone followed by hydrogenation is not an attractive route to glycerol synthesis. While the hydrogenation step was shown to be easy and satisfactory, the selective formaldehyde condensation to C_3 sugars proved to be impossible to control This, coupled with a lack of a low carbon number sugar separation process does not recommend this route as a physicochemical method for food synthesis from metabolic wastes

The alternate route to edible food production, namely condensation of formaldehyde to formose sugars (predominantly in the C_5-C_6 range) followed by hydrogenolysis to afford glycerol and propylene glycol, was also studied and shown to be feasible However, a great deal more work is required on all aspects of the process before it can achieve practical value Development of a more detailed understanding of the kinetics of the formose reaction is essential before good process control can be achieved. Unfortunately, because of the complexity of the system, the study of its kinetics constitutes a formidable task in itself requiring a sizable amount of further work and time Crude and approximate (perhaps meaningless) rate data on the formaldehyde condensation reaction can be obtained by making some simplifying assumptions (e g , ignoring reverse and other competing reactions), but accurate information requires much more effort than has been alloted to it thus far From a practical point of view, the usefulness of the formose reaction lies in

its potential to produce reasonable quantities of C_3 polyols after hydrogenolysis Reasonable estimates of the C_5-C_6 sugar content in any individual formose mixture can now be made by comparing its C_3 polyol yields with those obtained, under similar experimental conditions, from neat C_5-C_6 carbohydrates On this basis, all kinetic parameters controlling the formaldehyde condensation could be varied and their effects evaluated as a function of the ultimate combined yield of glycerol and propylene glycol produced after the catalytic reductive cleavage step

Optimum conditions for the hydrogenolysis reaction must still be developed. Although the feasibility of this step was demonstrated, the low selectivity of the reaction to edible polyols recommends that additional studies be carried out to improve the yields of glycerol and propylene glycol The hydrogenolysis reaction, as it now stands, i e , cleavage of C_5-C_6 sugars to C_3 fragments followed by reduction, suffers from competition with the hydrogenation of the starting material. While catalysts could be designed so their activity towards the hydrogenation reaction of C_5-C_6 carbohydrates, if any, be minimum relative to its C_5-C_6 cleavage process and C_3 hydrogenation, we do not recommend such an approach Rather, we favor the design of a catalyst system which would rapidly reduce the starting material to C_5-C_6 polyols followed by cracking to glycerol and propylene glycol, a system which we suspect will be more efficient Since relatively little is known about this reaction, we recommend research on its kinetics using the best catalyst so conditions will be discovered under which maximum edible triols will form at the highest conversion level of entering carbohydrate Hopefully, the potential catalyst will, in

addition to improving the selectivity of the system toward C_3 polyols, prevent formation of undesirable by-products and particularly those decomposable ones which lead to contamination of glycerol during the distillation process The resulting improved selectivities and the absence of decomposable products should simplify the separation studies and should provide the necessary information required for the design of the distillation section of the edible polyol synthesis unit.

IV. RESULTS AND DISCUSSION

A. Demonstration Glycerol Synthesis Unit

1 Design and Construction of the Unit

A Demonstration Glycerol Synthesis Unit was designed and constructed A schematic flow plan for the Demonstration Glycerol Synthesis Unit is shown in Figure 2. In the unit, a formaldehyde in water solution is fed to a catalytic condensation unit where partial formaldehyde conversion is effected to produce a mixture of C_6, C_5 and C_4 sugars. Following the condensation section, the condensation reaction in the product is quenched by a combination of cooling and/or catalyst removal The quenched product stream then enters a separation section where the unreacted formaldehyde is removed via low pressure flash fractionation The resultant formaldehyde free sugar mixture in water is then fed to a flow Hydrogenolysis unit The product from the hydrogenation reactor is then passed into a gas-liquid separator where unconverted H_2 is removed for simulated recycle to the reactor The product polyol mixture in water can then be fed to a separation section where the various polyols can be separated via fractional distillation to produce a glycerol product stream

The most demanding portion of the Demonstration Synthesis Unit is the Hydrogenolysis Reaction Section which is designed for operating pressures up to 2,000 psig and 400°F It is planned to use hydrogen pressures considerably lower than 2,000 psig to effect sugar hydrogenolysis, however, it was felt that designing and constructing a unit with this capability was important to the success of the project

A schematic of the Hydrogenolysis Reaction System is shown in Figure 3. A detailed drawing of the Hydrogenolysis Reactor itself is shown in Figure 4 Details of the preheater used to raise the temperature of the entering sugar/water solution and the feed hydrogen is shown in Figure 5

In the Hydrogenolysis Reaction section of the unit the sugar/water solution from the Formaldehyde Condensation Reaction section is fed to a Lapp pump where its pressure is raised up to 2,000 psig High pressure hydrogen is supplied from a cylinder in the Demonstration Unit, in an actual unit a recycle compressor would raise the pressure of the hydrogen to 2,000 psig The separate sugar/water and H_2 streams are heated to reactor temperature in a dual coil preheater (Figure 5) before being fed to the Hydrogenolysis Reactor itself through a high pressure tee point The reactor itself is a downflow, fixed bed catalytic reactor (Figure 4) The grannular catalyst is supported on a sintered disk which allows the effluent to pass while retaining the catalyst Separate thermocouples are provided to measure the temperatures of the inlet sugar/water solution, feed hydrogen and catalyst bed temperature The reactor effluent then passes through a pressure control valve (Mitey-Mite valve) which drops the pressure to essentially atmospheric The total effluent then enters a gas/liquid separator In an actual glycerol unit the unconverted hydrogen would be recycled back to the inlet gas compressor In the Demonstration Unit, the unconverted hydrogen is vented for convenience The product polyol mixture from the bottom of the gas liquid separator can then be fed to a distillation column for separation of the glycerol

In order to qualify the Hydrogenolysis Unit for high pressure service, a number of safety features required in the petroleum industry had to be incorporated into the unit design These safety features involved the installation of high pressure "pop" safety relief valves, check valves (a valve permitting only uni-directional flow) and a velocity check valve (a valve that stops high pressure gas flow in the event of a sudden gas flow surge caused by rupture of the unit) Details of these design features are shown in Figure 3. The unit was inspected by a team of safety experts and was judged capable of operation

A photograph of the High Pressure Hydrogenolysis Section is shown in Figure 6, and a photograph of the Formaldehyde Condensation Section is shown in Figure 7

FIGURE 3

DEMONSTRATION GLYCEROL UNIT - HIGH PRESSURE HYDROGENOLYSIS SECTION

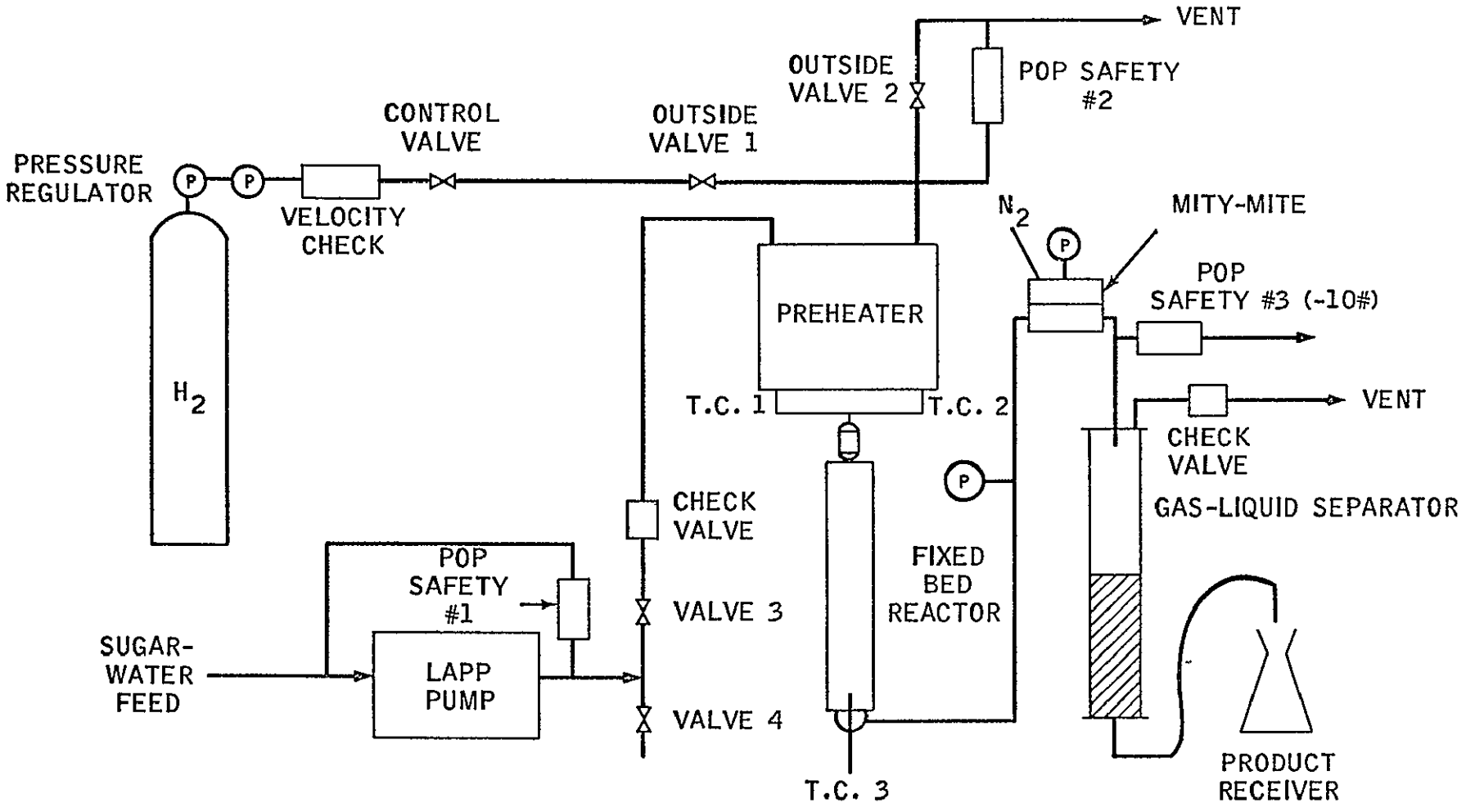
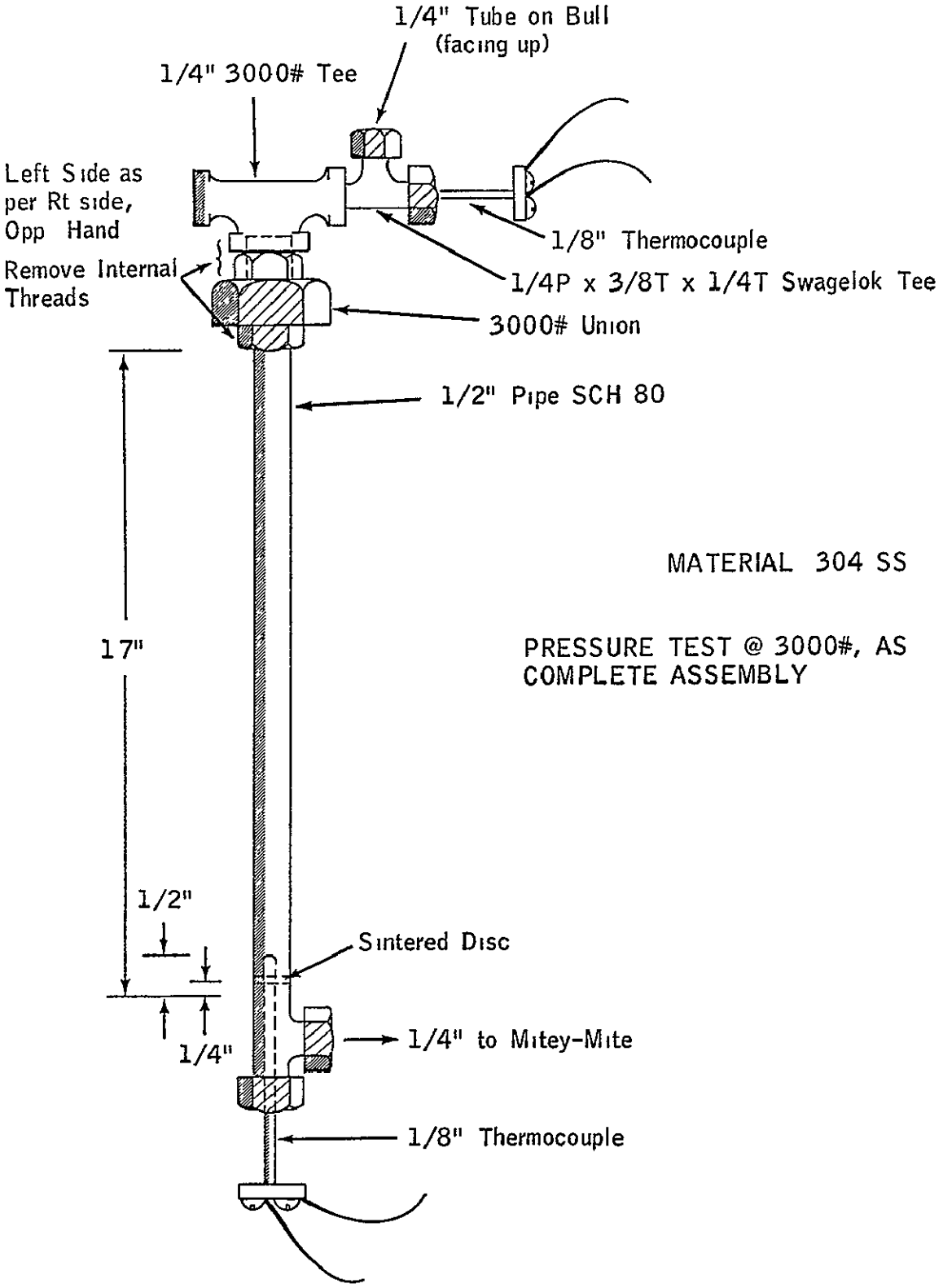
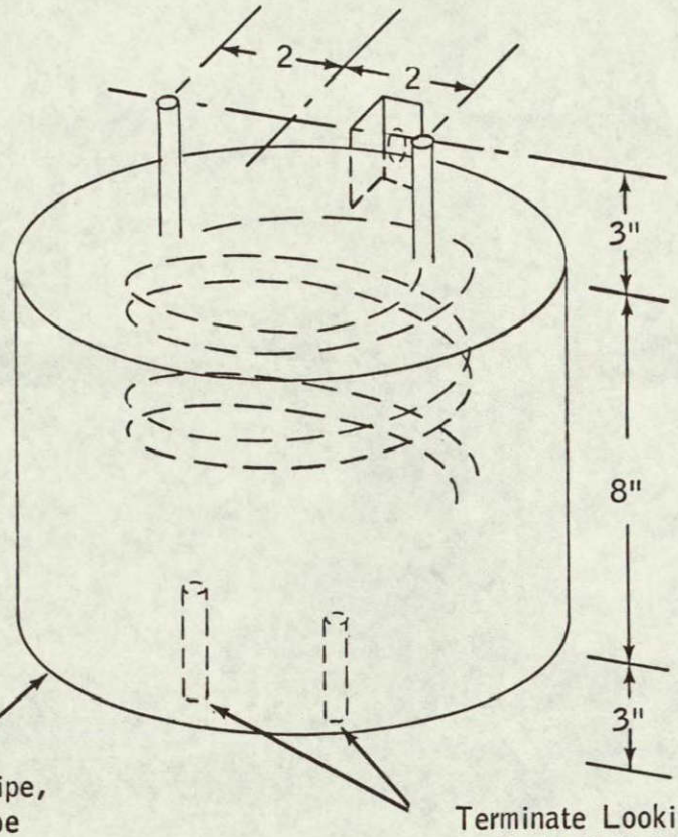


FIGURE 4



HYDROGENOLYSIS UNIT

FIGURE 5

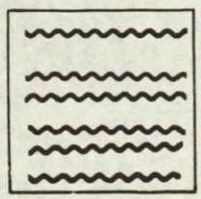


Weld Support
Top & Btm on 8" Pipe,
W/Btm Closure, Tube
Exits Sealed F/Aluminum
Block Casting

Terminate Looking Down 8 Turns in Each Coil 6" Diam. Coils of 1/4" Tubing on 3/4" Vertical ℄ Spacing; make up to Reactor, SH. 1

GENERAL NOTES

- Fabricate 2 coils and install in pipe form f/aluminum block casting, by others. Cap tubing ends
- Wrap W/3 500 W Briskeat tapes, Insulate F/500°F service, and terminate leads on each tape W/identification.
- Parallel connect 1 and 3 on variac/ switch, manual input
- Tape 2 on Gardsman controller



PREHEATING UNIT FOR HYDROGENOLYSIS UNIT

FIGURE 6

HIGH PRESSURE HYDROGENOLYSIS UNIT SECTION

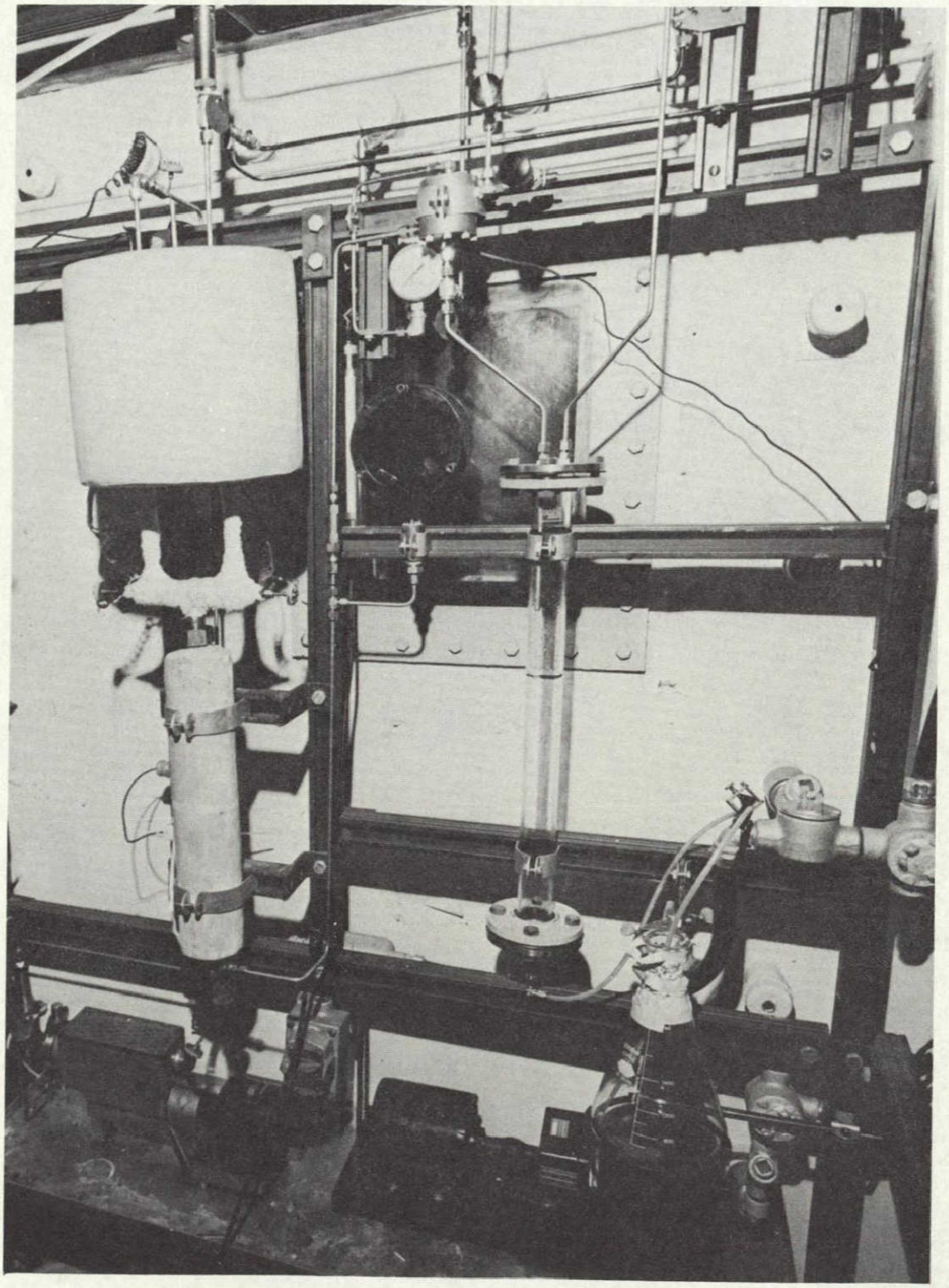
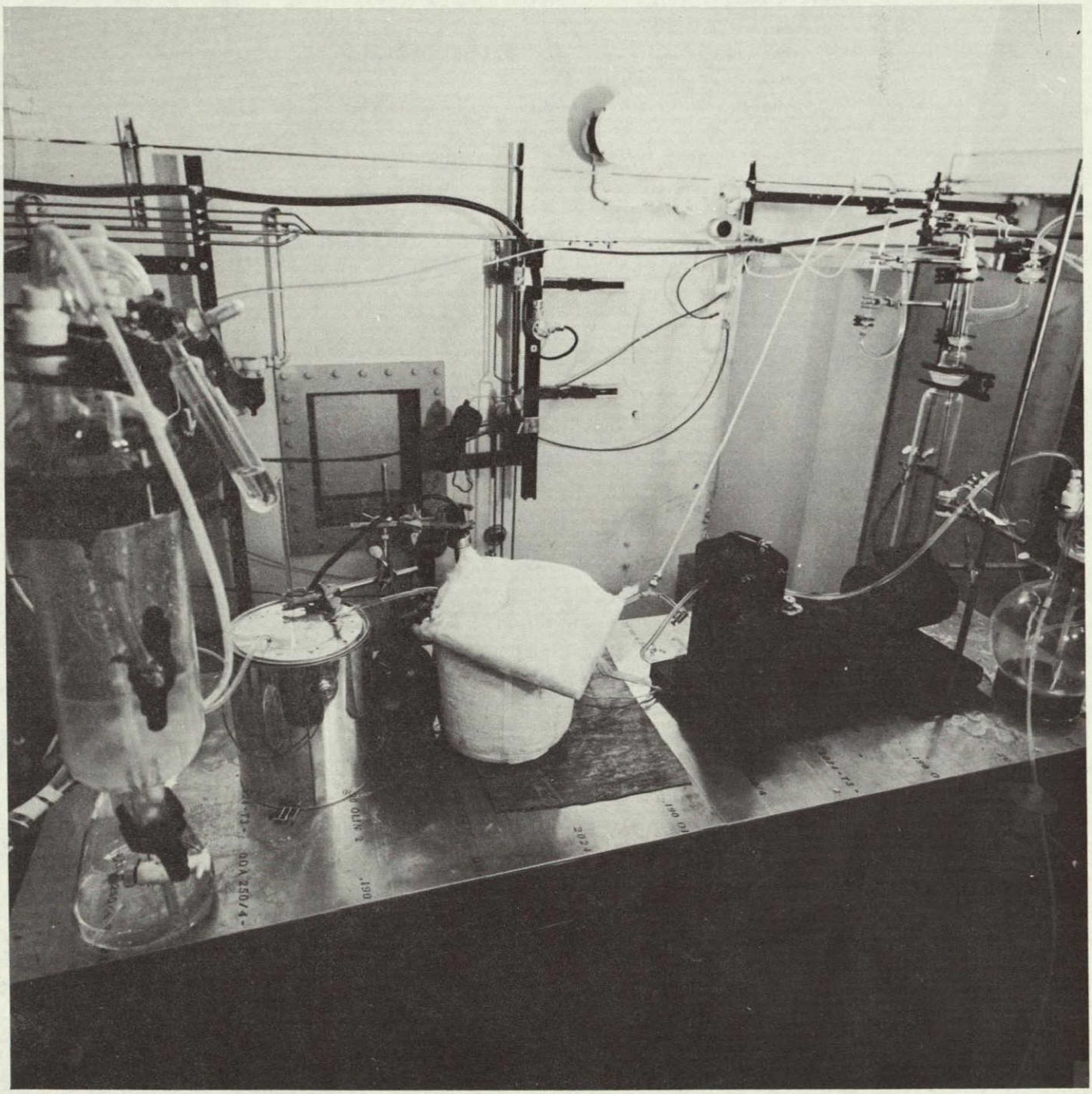


FIGURE 7

FORMALDEHYDE CONDENSATION UNIT SECTION



2. Operation and Evaluation of the Unit Performance

The High Pressure Hydrogenolysis Section of the Glycerol Demonstration Unit was first given a unit pressure test. The object of this test was to determine if the unit was leak tight before high pressure hydrogen was admitted. High pressure hydrogen represents a serious safety hazard in a leak situation because of the high flammability and explosion hazard, when it is mixed with air. In addition, because of its negative Joule-Thompson coefficient, it is possible for high pressure hydrogen leaking to low pressure to heat itself to the point where it will undergo combustion and/or explosion. The pressure test-procedure is shown in Table 1.

After the pressure test was successfully completed, a shakedown run was carried out with the High Pressure Hydrogenolysis section of the Glycerol Synthesis Demonstration Unit. The object of this run was to demonstrate that the major unit components such as the unit Mity-Mite would operate properly before actually charging a catalyst to the unit and admitting a sugar solution feed. The shakedown run procedure is shown in Table 2.

The shakedown run operation indicated that the Teflon seat in the mity-mite failed to operate properly. It was charged to a Buna N seat which is less sensitive to small particles (i.e. potential catalyst attrition particles) in the reactor effluent. The run procedure adopted is shown in Table 3.

Following the shakedown run, a physical mixture of the following catalysts was charged to the Hydrogenolysis Reactor

22g 15% Ruthenium on carbon

8g FC-13 20% CaO/Al_2O_3

A hydrogenation/hydrogenolysis catalyst (Ru/C) was mixed with a formaldehyde condensation catalyst (CaO/Al_2O_3) since earlier studies indicated that low pressure hydrogenolysis of C_6 sugars occurred via, first, a reverse condensation to lower sugars, followed by hydrogenation of the sugars to a low carbon number polyol, rather than via a direct hydrogenolysis of the C_6 sugar (i e rupture of the C-C bond in the sugar under the influence of H_2, followed by a hydrogenation of the fragments) Two runs were carried out with the mixed catalyst using formaldehyde condensation product sugar solution 105 or the feed Conditions were

	Preheater		Reactor	
Run	Sugar solution °F	H_2 °F	Temperature °F	Pressure psig
491-22	100	100	200	500
491-24	100	100	250	300

The product from both runs was a clear, colorless liquid After evaporation of water, the product from Run 491-22 was a viscous dark liquid A GC of this material from 491-22 is shown in Appendix 88 An examination of this GC trace indicates no presence of glycerol After evaporation, the product from run 491-24 was a yellow residue A GC of the residue is shown in Appendix 89 Examination of this GC trace indicated no presence of glycerol The compounds present appeared to

be of the type present in the feed sugar solution, although some hydrogenation of the higher carbon number sugars to polyols may have occurred Thus, hydrogenolysis of the feed sugar solution did not occur

An evaluation of the High Pressure Hydrogenolysis Unit results indicates that the unit performed well, but that the Ru/C plus CaO/Al_2O_3 catalyst was incapable of effecting a Hydrogenolysis reaction at the relative low hydrogen pressures used in these runs, i e 300 and 500 psig. Since other test results have indicated that Ru/C catalysts are quite active for the hydrogenation of C_2 and C_3 sugars at very low hydrogen pressures, presumably, the CaO/Al_2O_3 heterogeneous catalyst failed to effect the reverse condensation reaction which a homogeneous $Ca(OH)_2$ catalyst effects readily Two approaches are possible to overcome this lack of catalyst activity First, develop an active reverse formaldehyde condensation catalyst, or second, operate the Unit at much higher hydrogen pressures with an active Hydrogenolysis catalyst so as to effect a direct cleavage of the C-C bonds under the action of the hydrogen, rather than carry out the bore catalyzed reverse formaldehyde condensation

Table 1

Unit Pressure Test Procedure

(1) Close outside valves 1, 2, and 4, open valve 3

(2) Set Mity-Mite for 500#

(3) Feed water to pump

(4) Start pump and observe for H_2O leaks

(5) When unit is tight, raise pressure to 1,000# Check for leaks

(6) If tight, raise preheater temperature so that T_1, T_2, and T_3 are in the 300-350°F range

Table 2

Shake-Down Run Procedure

(1) Purge unit with N_2

(2) Open valve 3, close valves 1, 2, and 4

(3) Set Mity-Mite for 500#

(4) Set H_2 control valve for desired value

(5) Start Lapp pump at desired rate, collect H_2O in seapartor

(6) Open valve 1, start H_2 flow

(7) Raise preheater and reactor temperature to 200°F

Table 3

Run Procedure

(1) Charge catalyst-close unit

(2) Purge Unit with N_2

(3) Close valves 2, 4, open valves 3 and 1

(4) Set Mity-Mite for operating pressure Set H_2O level in Sep

(5) Introduce H_2 at 100 psi Check for leaks around reactor fittings

(6) Close valve 1 Set H_2 pressure to 550 psi Set control valve

(7) Open valve 1--starting H_2 flow

(8) Start pump at proper setting

(9) Raise preheater temp to ~200°F and reactor temp to 200°F Then raise temperature to desired settings

(10) Make 15 min run sheet recordings

B Formaldehyde Condensation Studies

The object of our study of the formaldehyde condensation reaction is to develop conditions (temperature, catalyst and co-catalyst concentrations, and contact time) under which maximum conversion of starting material to C_5-C_6 carbohydrates can be obtained Such a product mixture would presumably undergo, under the proper conditions, hydrogenolysis to edible polyols, i e , glycerol and propylene glycol Thus, experiments were designed in which catalyst and co-catalyst concentrations as well as contact time were varied and their results are summarized in Table 4 In this study, use was made of a batch reactor into which an 8% formaldehyde solution was introduced and heated under nitrogen until the temperature reached 60°C $\pm$ 1°C The catalyst and co-catalyst were then simultaneously added and the reaction begun Upon completion, the reaction mixture was cooled and calcium hydroxide was precipitated as the oxalate salt Following deionization, the solution was concentrated under vacuum Trifluoracetyl derivatives of the mixture were made and gas-liquid chromatographic analysis was performed using the internal standard method (16), glycerol being the internal standard used Peak areas were measured with a planimeter and the composition of the mixture was obtained using the following equation

$$\% \text{ solute}_1 = f_1 A_1 R/A_s$$

where f_1 is the area factor (mg/unit area) of component 1, A_1 is the measured area of component 1, R the percent internal standard added to the sample and A_s is the measured area of the internal standard added

It is appropriate to mention that of all carbohydrate trifluoroacetyl derivatives those of erythroses were the only species which, when they appeared in the chromatogram (sometimes they did not), yielded ill-defined broad peaks, hardly gaussian in shape and barely above the base line Therefore their absence in the chromatogram does not necessarily mean their lack of formation in the formaldehyde condensation reaction Chromatograms of all formaldehyde condensation runs appear in Appendices 1 through 7

Data on the formose reaction reveal that, under the experimental conditions used, the system requires some control if the C_5-C_6 sugar yield is to be maximized The yield in C_5-C_6 carbohydrates was found to be highest at complete or near complete formaldehyde conversion (see Table 4) However, at these conversion levels, formation of undesirable products, e g , saccharinic acids, begins to take place as a result of alkali promoted degradation of high carbon number sugars It is not known whether these acids can be hydrogenolyzed to yield glycerol and propylene glycol, but even if they could, they would most likely give rise to other undesirable products as well At intermediate and low formaldehyde conversion levels, mostly trioses and pentoses are present with sometimes a small or trace amount of tetroses

In addition to giving rise to undesirable products, runs with high formaldehyde conversion (451-65 and 451-66) exhibit an interesting feature, namely the production of glycolaldehyde Formation of the latter can be explained in terms of a reverse aldol condensation from higher carbohydrates, i e , tetroses, pentoses, and hexoses Dealdolization of carbohydrates in the presence of alkali has been proven (17-20) for glucose and fructose and found to yield trioses Our own alkali co-catalyzed hydrogenolysis work on pure C_5-C_6 carbohydrates to yield

Table 4

Formaldehyde Condensation Runs

Run No	$Ca(OH)_2$ Concentration Mole/l	Glycolaldehyde Concentration x 10^2 Mole/l	Temp °C	Run Time Minutes	/ Conversion*	Unreacted Formaldehyde	Product Distribution, Wt / ± 05						
							C_2	C_3	C_4	C_5	C_6	Other	Material Balance
451-65	1 62	0 15	60	10	98 4	1 6	4 7	4 1	2 3**	24 3	10 0	16 5(a)	63 4
-66	1 62	0 15	60	15	100	0	3 5	10 0	Trace	12 2	5 0	18(a)	48
-67	1 62	0 15	60	5	40 4	59 6	--	5 2	--	4 2	--	--	69 4
-72	0 81	0 15	60	10	11 0	89	--	9 4	--	8 5	--	--	106 9
-73	0 81	0 15	60	20	31 1	68 9	1 2	12 4	Trace	9 0	--	--	91 5
-74	0 81	0 15	60	15	24 8	76 2	--	3 8	--	6 7	--	--	86 7
-81	0 81	0 42	60	10	60 7	39 3	--	8 7	Trace	12 3	--	--	60 3

*Based on sodium sulfite titration for formaldehyde and reported to the nearest 0 1

**Estimated

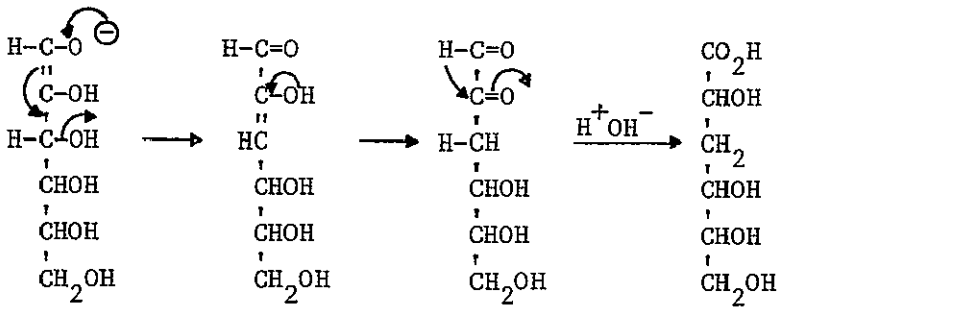
(a) uncorrected - unknown species appearing beyond C_6-C_7 and suspected to be saccharinic acids

ethylene glycol and C_3 polyols is a further proof that high carbon number sugars constitute one possible source for glycolaldehyde production Dealdolization of high carbon number carbohydrates may, in our opinion, be responsible not only for glycolaldehyde formation and triose enrichment at high formaldehyde conversion levels, it may also explain the non-straightforward correlation between percent conversion and selectivity to C_5-C_6 carbohydrates Indeed with all sorts of equilibria and recombination reactions taking place and with concentrations of various species changing, it is difficult to conceive of a straightforward correlation between conversion and C_5-C_6 yield The situation is further complicated by the fact that at high conversion levels (as in Runs #451-65 and $451-66), species of lower

$$C_5 \rightleftharpoons C_3 + C_2$$
$$C_6 \rightleftharpoons C_3 + C_3$$
$$C_6 \rightleftharpoons C_4 + C_2$$
$$C_4 \rightleftharpoons C_2 + C_2$$
$$C_2 + C_3 \rightleftharpoons + C_5$$
$$C_3 + C_3 \rightleftharpoons + C_6$$
$$C_2 + C_2 \rightleftharpoons + C_4$$
$$C_2 + C_4 \rightleftharpoons + C_6$$

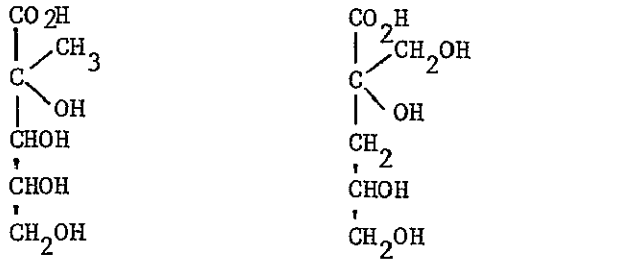
volatility than C_6-C_7 sugars begin to form For lack of any positive evidence as to the nature of these species, we will content ourselves with speculation based on the known chemistry of carbohydrates It is our belief (and we intend to prove it later) that the species in question correspond to various saccharinic acids, i.e., meta-saccharinic, isosaccharinic, etc , which have different volatilities

and whose derivatives, therefore, must exhibit different degrees of volatility Furthermore, because of their acidic nature, hydrogen bonding due to the presence of a carboxylic proton will tend to diminish their volatilities relative to the non-hydrogen bonding C_5, C_6 and C_7 carbohydrate trifluoroacetates As to their formation, it can be explained in terms of the Isbell mechanism (21) which involves the following successive steps (1) the formation and ionization of an enediol, (2) the β-elimination of a hydroxyl group, (3) rearrangement to an α-dicarbonyl intermediate, and (4) a benzilic acid type of rearrangement to the saccharinic acid



Metasaccharinic acid

Isosaccharinic and saccharinic acids have the following structures



Saccharinic acid Isosaccharinic acid

Kenner, et al (17,22,23) has obtained saccharinic acids from alkali degradation at room temperature of glucose, fructose and from a number of their derivatives This being the case, the formose reaction will have to be controlled so as to obtain conversion levels at which no such depletion of high carbon number carbohydrates (via alkali degradation) will occur to any large extent

C Hydrogenolysis Studies

1. Hydrogenolysis of Neat Carbohydrates

From the reported work described in the Introduction on the hydrogenolysis of carbohydrates, it appears very clear that glycerol and 1,2-propylene glycol production is very sensitive to the nature of the catalyst as well as other parameters (pressure, temperature, etc) governing the hydrogenolysis reaction It was, therefore, our judgement that a study be carried out on the hydrogenolysis reaction of pure C_5-C_6 carbohydrates so that the effects of the catalyst composition, hydrogen pressures, and temperature on its kinetics and on its product distribution be known Reactions were run in a low pressure Parr hydrogenator and a high pressure autoclave using C_3, C_4, C_5 and C_6 sugars as starting materials In both systems, an aqueous solution of the carbohydrate is introduced into the reactor followed by the addition of the catalyst (and co-catalyst when applicable) The system is then vented and pressured to the desired initial pressure after which the heater is turned on and the reaction is begun Hydrogen consumption is followed by recording the pressure drop as a function of time When hydrogen uptake ceases or tapers off for a substantial length of time, the reaction is stopped and the product mixture analyzed in the manner described in the experimental section of this report The results of this study are summarized in Tables 5 and 6 and the effects of catalyst type, carbohydrate structure and hydrogen pressure on glycerol and propylene glycol yields will be described below Gas chromatograms of the various runs appear in Appendices 8 through 53

Table 5

Carbohydrate Hydrogenolysis Runs

Run #	Starting Material and Concentration Mole/l	Catalyst Type and Amount	Co-Catalyst [$Ca(OH)_2$] Concentration-Mole/l	Temp °F	Initial H_2 Pressure Psig	H_2 Uptake Psig	H_2 Uptake Atmosphere
491-2	Glucose-3 7	Copper chromite-16 65 g	0	415	1500	225	15 31
-4	Glucose-3 7	Copper chromite-16 65 g	0	415	1850	200	13 61
-5	Fructose-3 7	Copper chromite-16 65 g	0	310	1800	190	12 93
-6	Glucose-1 108	5% Ru/C-8 g	0 054	200	300	70	4 76
-7	Glucose-1 108	5% Ru/C-4 g	0 108	200	300	30	2 04
-8	Glucose-1 108	5% Ru/C-8 g	0 054	200	500	120	8 16
-10	Fructose-0 664	5% Ru/C-8 g	0 054	200	500	100	6 80
451-54	Fructose-0 55	35% Ru/Al_2O_3	0	200	75	23	1 56
-58	Fructose-0 55	5% Ru/C-2g	0 068	200	75	65	4 42
-61	Fructose-0 55	5% Ru/C-2 g	0	200	75	46	3 13
-78	Sorbitol-0 54	5% Ru/C-2 g	0 068	200	81	0	0
-84	Formose mixture-0 55	5% Ru/C-2 g	0.068	200	75 8	32	2 38
-86	Glucose-0 55	Esso 500-2 g	0	200	75	24	1 63
-87	Glucose-0 55	Esso 500-2 g	0 068	200	75	12	0 82
-88	Glucose-0 55	Esso 500-2 g	0	75	74 2	9 5	0 65

Table 5 (Cont'd)

Run No	Starting Material and Concentration-Mole/l	Catalyst Type and Amount	Co-Catalyst [$Ca(OH)_2$] Concentration-Mole/l	Temp °F	Initial H_2 Pressure-Psig	H_2 Uptake	
						P-ig	Moles
451-90	Arabinose-0 0668	5% Ru/C-0 5 g	0 017	200	75	14	0 019
451-91	Xylose-0 0668	5% Ru/C-0 5 g	0 017	200	74 9	13 9	0 019
451-92	Ribose-0 0668	5% Ru/C-0 5 g	0 017	200	77	14 6	0 020
451-93	Erythrose-0 0668	5% Ru/C-0 4 g	0 017	200	75	8 8	0 010
451-94	Glyceraldehyde-1 112	5% Ru/C-0 5 g	0 017	200	74 1	10 9	0 015
451-95	Dihydroxyacetone-1 112	5% Ru/C-0 5 g	0 017	200	75	9 3	0 013
491-12	Fructose-1 104	5% Ru/C-8 g	0 056	200	1000	250	0 412
491-13	Glucose- 1 104	5% Ru/C-8 g	0 054	200	1000	285	0 473

Table 6

Carbohydrate Hydrogenolysis Runs

Run No	H_2 Uptake Moles	Theoretical[a] H_2 Uptake Moles	% Conversion	Product Distribution, Wt / Glycerol	Propylene Glycols	Ethylene Glycol	Other Wt %
491-2	0 29	0 925	31 35	0	5 9 0 22	3 37	C_2 sugar-0 41 trioses-7 6 C_6 carbohydrates and polyols-38 erythritol-1 69 acids-15**
-4	0 26	0 925	28 10	0	1 63	3 04	trioses-3 C_5 polyol-0 18 acids**-19 C_6 carbohydrates and polyols-40 lactic acid-0 7
-5	0 28	0 925	30 27	Trace	0	0	trioses-8 09% pentoses-1 45 C_6 carbohydrates and polyols-73
-6	0 122	0 277	44 04	12 6	2 97	2 96	trioses-12 erythritol-2 11 1,2,4-butane triol-2 67 C_6 sugars and polyols-51
-7	0 05	0 277	18 05	3 5	0 72	2 51	C_6 sugars and polyols-72
-8	0 21	0 277	75 8	20	1 86 6 72	6 48	erythritol-3 25 1,2,4-butane triol-5 10 C_6 sugars and polyols-55
-10	0 174	0 166		15 2	5 76	3 73	trioses-13 erythritol-1 12 1,2,4-butane triol-0 78 C_6 sugars and polyols-41
451-54	0 022	0 110	20 0	0	0	0	suspected trioses-27 C_6 sugars and polyols-63
-58	0 060	0 110	54 54	10 17	4 52	1 45	trioses-7 1,2,4-butane triol-3 12 C_6 sugars and polyols-47 8
-61	0 043	0 110	39 09	0	0	0	trioses-1 85 C_6 sugars and polyols-74
-78	0	0 110	0	0	0	0	C_6 sugars and polyols-100

**uncorrected unknown suspected to represent saccharine acids

(a) based on hydrogen uptake for complete hydrogenolysis, i e , 2 moles of H_2 to one mole of carbohydrate

Table 6 (Cont'd)

Run No	H_2 Uptake Moles	Theoretical[(a)] H_2 Uptake-Moles	% Conversion	Product Distribution - Wt %			Other, Wt %
				Glycerol	Propylene Glycol	Ethylene Glycol	
451-84	0 0323	0 088	36 70	10 82	2 26	9 3	Erythritol-166 C_2 sugar trace pentoses-13 C_6 sugars and polyols-49 C_6 sugars and polyols-49
451-86	0 022	0 110	20 0	0	0	0	Suspected trioses-20 C_6 sugars and polyols-57
451-87	0 011	0 110	10 0	0 73	0	0	Suspected trioses-44 C_6 sugars and polyols-39
451-88	0 088	0 110	88	0	0	0	Suspected trioses-33 C_6 sugars and polyols-58
451-90	0 019	0 0334	56 94	19 15	Trace	3 34	Arabinose-4 85 C_5 polyol-39 19 C_6 polyols-11 8 Butanetriol-2 80
451-91	0 019	0 0332	56 60	9 53	Trace	4 06	Xylose-1 86 C_5 polyol-34 69 C_6 polyol-12 53 Butanetriol-0.27
451-92	0 020	0 0332	59 64	4.39	0	1.46	C_5 polyols 22 05 C_6 polyols 1 68 Butanetriol-1 53
451-93	0 010	0 0332	30 90	1 48	Trace	3 34	C_4 polyol 7 62 Glyceraldehyde-2 11

(a) Based on hydrogen uptake for complete hydrogenolysis, i e , 2 moles of H_2 to one mole of carbohydrate

Table 6 (Cont'd)

Run No	H_2 Uptake Moles	Theoretical[(a)] H_2 Uptake-Moles	% Conversion	Product Distribution - Wt % Glycerol	Propylene Glycol	Ethylene Glycol	Other, Wt %
451-94	0 015	0 0278	53 24	17 06	1 13	1 61	C_5 polyols 1 41 C_6 polyosl 2 09
451-95	0 013	0 0278	45 32	38 36	0 37	Trace	C_5 polyols 19 26 C_6 polyols 2 82 C_4 polyol 4 49 Butanetriol 6 10
491-12	0 412	0 555	74 76	17 45	2 79	1 59	C_5 polyols 4 04 C_6 polyols 28 06 C_4 polyol 1 10 butanetriol 2 10 dihydroxyacetone 1 55
491-13	0 473	0 555	85 22	8 65	1 67	0 64	C_5 polyols 1 77 C_6 polyols 19 43• C_4 polyol 1 02 butanetriol 2 0

*Based on hydrogen uptake for complete hydrogenolysis, i e , 2 moles of H_2 to one mole of carbohydrate

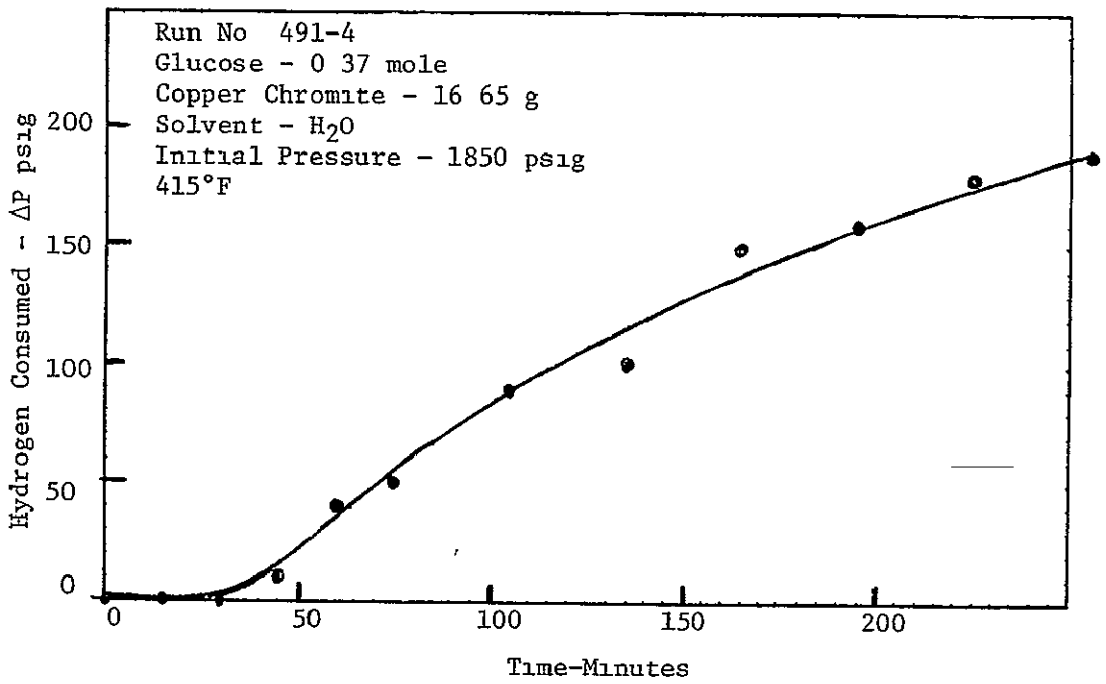
a. Effect of Catalyst Type

Four catalysts were evaluated in our preliminary investigation of the hydrogenolysis reaction, 5% Ru/C, 35% Ru/Al_2O_3, Esso 500 (developed by Esso Research and Engineering) and copper chromite which is reportedly selective to glycerol The latter did not prove to be true under our experimental conditions Figure 8, which shows the rate of hydrogen consumption as a function of time, also points to a short induction period At up to 1850 psig pressure and 415°F, 31% conversion was observed but only 5 9% of 1,2-propylene glycol and 0 22% of 1,3-propylene glycol were obtained and no glycerol formation was formed

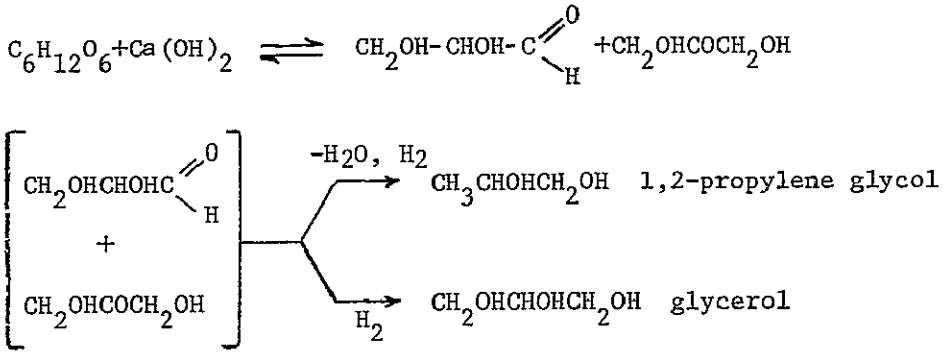
Ruthenium on carbon was found to be quite effective when used in conjunction with $Ca(OH)_2$ as co-catalyst Reasonable yields of glycerol (Table 6) and propylene glycols were obtained from both glucose and fructose The remaining two catalysts evaluated in this study had a high ruthenium content (35%) and while they did not produce glycerol, they showed some activity towards hydrogenation of high carbon number carbohydrates (see Appendices 36 and 37) On the basis of these early results, 5% Ru/C used in conjunction with $Ca(OH)_2$ was the catalyst of choice and was employed to obtain all data on the hydrogenolysis reaction of carbohydrates

Figure 8

Rate of Hydrogen Uptake



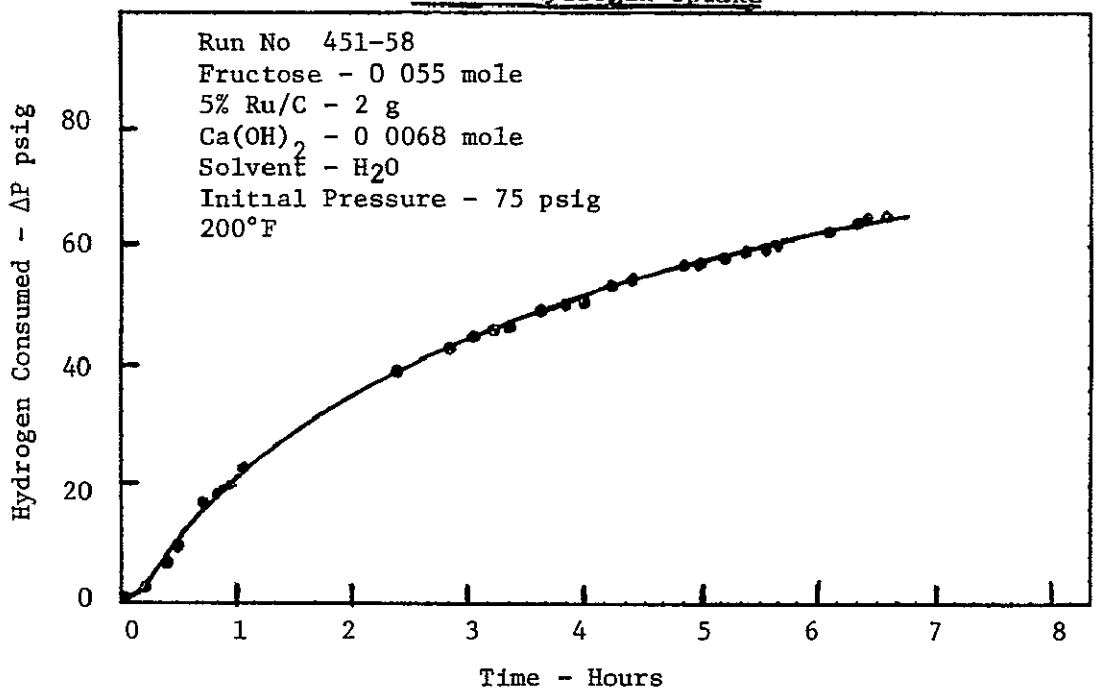
Formation of glycerol and propylene glycol from high carbon number sugars can be visualized to take place, in the case of Ru/C and $Ca(OH)_2$, via reverse aldol condensation followed by hydrogenation of the smaller fragments to yield glycerol and propylene glycol The presence of the



base is necessary to affect the reverse aldol condensation step and reactions (i e , 451-61) from which $Ca(OH)_2$ was excluded yielded no glycerol or propylene glycol and did not show any evidence for glyceraldehyde or dihydroxyacetone formation Moreover, from Figures 9 and 10, it can be seen that initial rate of hydrogenation of the C_6 carbohydrate with 5% Ru/C is quite fast (78% of fructose are hydrogenated after 40 minutes) in the absence of $Ca(OH)_2$ compared to the rate of hydrogen consumption in the system producing glycerol Also, under the experimental conditions used (5% Ru/C, $Ca(OH)_2$), C_6 polyol was not found to be an intermediate in the formation of glycerol or propylene glycol and run #451-78 shows just that When sorbitol was used as the starting material, hydrogen was not consumed (Figure 11) and the product mixture indicated no presence of C_3 polyols or trioses Another interesting aspect of the results obtained with this system (Ru/C and $Ca(OH)_2$) is that two reactions which were originally anticipated to compete with C_3 polyol formation did not appear to take place during hydrogenolysis or, if they did, not to any alarming

Figure 9

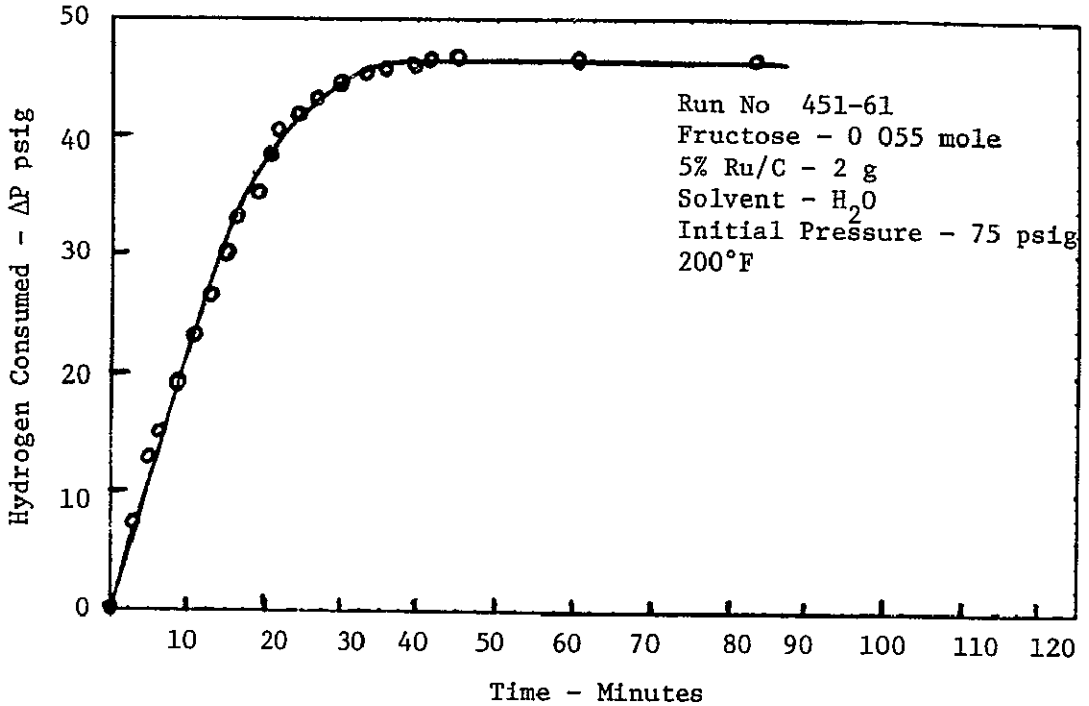
Rate of Hydrogen Uptake



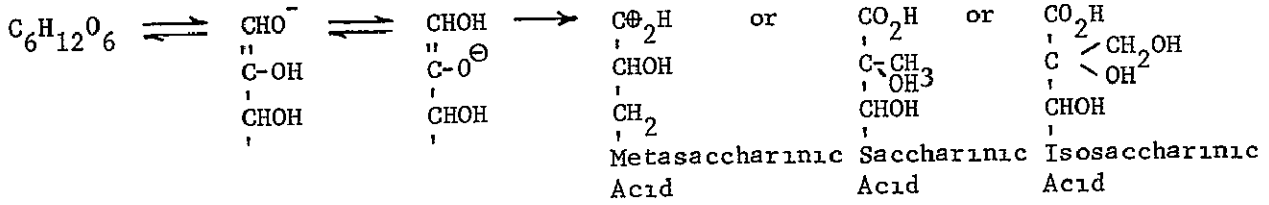
Rate of Hydrogen Consumption

Figure 10

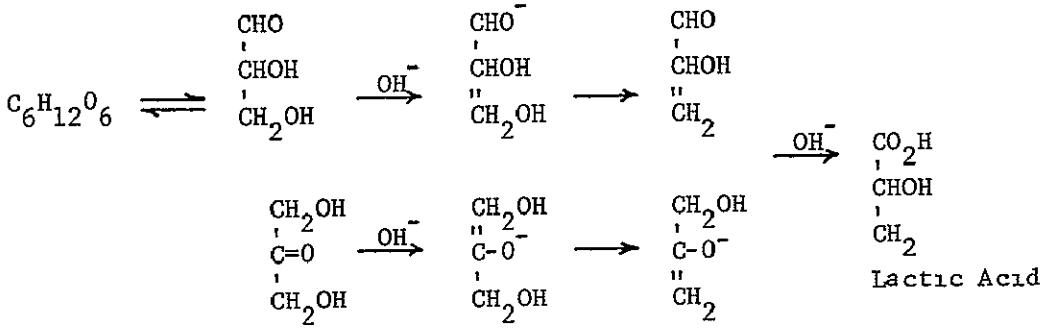
Rate of Hydrogen Uptake



extent One such reaction is the formation of saccharinic acids from gluocse and fructose in the presence of lime water reported (17,24) to take place even at 25°C via an enolate anion, as follows.



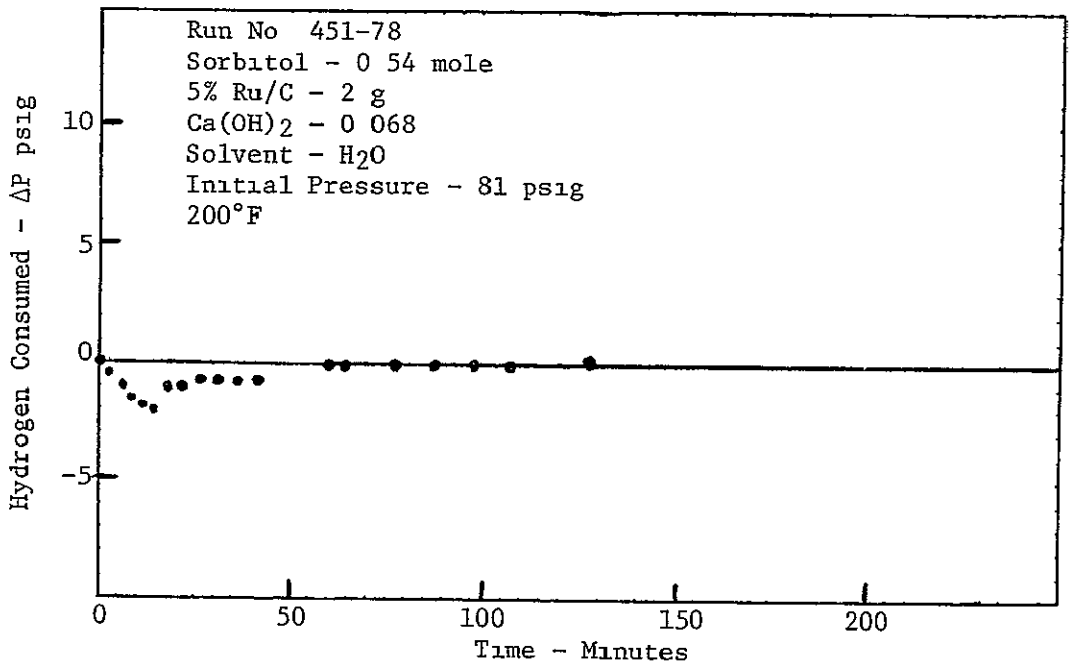
with preferential formation of one acid over the others depending on the structure of the starting material, and the position of substitution The other reaction anticipated to occur involves reaction of triose intermediates with alkali to form lactic acid. as shown bv the following equation



The concept of reverse aldolization to interpret sugar fragmentation which was first proposed by Bernier and Evans (18,19) has been utilized by others (17,20,25). Wolfrom and Schumacher (26), for instance, obtained DL-sorbose and DL-fructose from dealdolization of D-fructose to C_3 fragments followed by alkali catalyzed recombination of the latter Formation of trioses is further demonstrated by Kenner and Richards (17) who report predominance of lactic acid over saccharinic acids in the alkali degradation of glucose and fructose, via gly-

Figure 11

Rate of Hydrogen Uptake



ceraldehyde and dihydroxyacetone This, they postulate, is due to the greater simplicity of a reverse aldol reaction in comparison with the elimination of anion on which saccharinic acid depends Our results lend support to this hypothesis No saccharinic acid formation was observed and while we did not obtain lactic acid, the formation of the latter might be hindered because of the faster hydrogenation of the intermediate trioses to C_3 polyols Whether lactic acid versus saccharinic acid formation is due to pH effects or other is not yet known, but since lactic acid, glycerol and propylene glycol form only via trioses, the latter's intermediacy is proven by our results as well as those of Kenner and Richard (17)

Copper chromite has been reported (11) to yield 21% glycerol and 30% propylene glycol at 210 atmospheres, 250°C and ethanol as solvent In our hands, at 125 atmospheres and 212°C, we obtained an extremely small amount of propylene glycol (6% in one case and ∿2% in another) but no glycerol Both chromatograms of runs #491-2 and 491-4 showed peaks beyond those arising from the trifluoroacetyl derivatives of C_6 carbohydrates and polyols These species could very well arise from the above-mentioned less volatile saccharinic acids This remained to be verified Also, run #491-4 yielded some lactic acid and it appears that the very high hydrogen pressure (210 atmospheres) are necessary if C_3 polyols are to be obtained from C_6 sugars using copper chromite as catalyst This is undesirable for spacecraft application and efforts continue in the direction of discovering catalysts capable of activity at acceptable pressures and temperatures

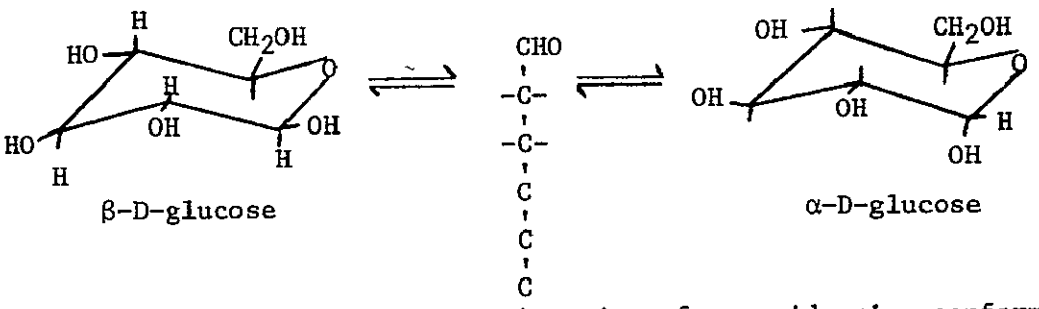
b Effect of Carbohydrate Structure

Tables 5 and 6 show a definite effect of carbohydrate structure on glycerol and 1,2-propylene glycol yields and this is particularly true for carbohydrates with the same carbon number, namely pentoses and hexoses.

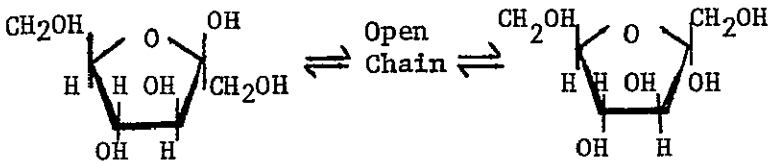
As discussed in the previous section, hydrogenolysis of C_6 sugars (and most likely C_5) to glycerol and propylene glycol proceeds via dealdolization to C_3 fragments followed by hydrogenation of the latter to yield C_3 polyols On the other hand, dealdolization in solution of a given optical isomer of a given carbohydrate is dependent on the following equilibria

cyclic structure (α-anomer) $\rightleftharpoons$ open chain structure $\rightleftharpoons$ cyclic structure (β-anomer)

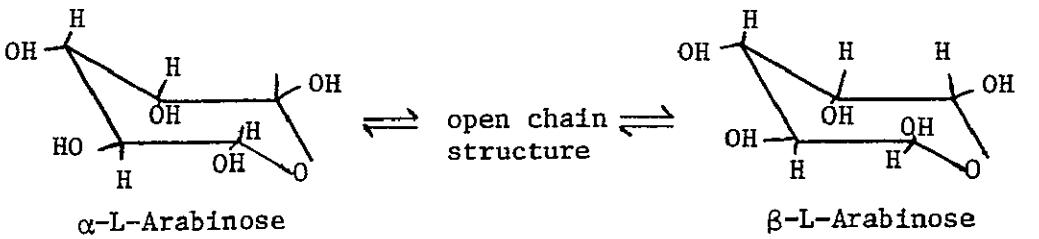
We suggest that it is the open chain form of the carbohydrate, in which the keto- or aldehydo- group of the given carbohydrate is free to allow enolization, which undergoes in the presence of $Ca(OH)_2$ reverse aldol condensation reaction. The concentration of the open structure, therefore, will be important in controlling the dealdolization process and is itself dependent on the cyclic structure(s) of the precursor carbohydrate in solution, the more stable the latter, the slower the equilibrium between open chain and cyclic structure and the slower the dealdolization The end result is lower yields of glycerol and propylene glycol Crystalline D-glucose exists, in its C_1 conformation, as the β-anomer where no instability factors exist (27). In solution, and particularly in the presence of an acid or a base, an equilibrium mixture of both α- (with the hydroxyl group on Carbon No 1 in an axial position) and β-anomeric forms obtains as a result of mutarotation, via an open chain structure



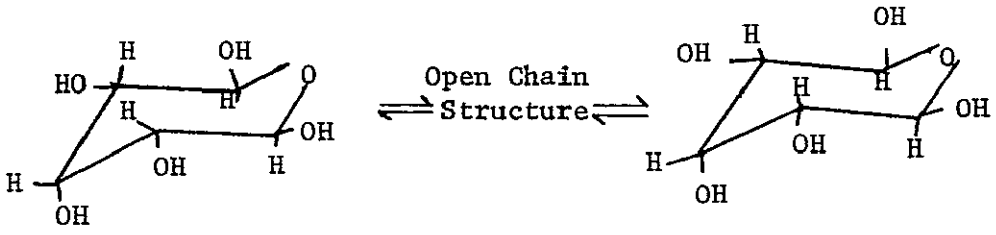
Fructose, a ketohexose, exists in a furanoside ring conformation and because of its ring strain would be expected to equilibrate with its



open chain keto-form to a larger extent than glucose. Also because it is a keto hexose, it possess 2α-positions for enolization. As a result, its dealdolization should proceed more rapidly than that of glucose, thus yielding more C_3 polyols than glucose. This is in fact what was observed. Under a given set of experimental conditions, D-fructose yielded larger quantities of glycerol and propylene glycol than did D-glucose, i.e., 17.45% and 2.79% versus 8.65% and 1.67%, respectively. This same argument of conformational stability can be extended to pentoses. According to Davidson (27), the preferred chair ring forms for L-Arabinose, D-Xylose and D-Ribose are of the 1C, C1, C1 types, respectively, and the more stable anomeric forms for the same three sugars are the α, β and β, respectively. From structural



considerations and conformational instabilities, one would predict that α-L-Arabinose and β-D-Ribose, each of which has a single hydroxyl group in an axial position (one axial hydroxyl group confers one instability unit to the conformer under consideration), would follow fairly much the same reaction



β-D-Ribose α-D-Ribose

path and would yield approximately the same amount of C_3 polyols. β-D-Xylose, on the other hand, free of any instability factors, would be expected to react slower than Arabinose or ribose and yield smaller quantities of C_3 polyols than the two other C_5 carbohydrates

The order observed, however, is α-L-Arabinose (19.15%) > β-D-Ribose (4.39%) > β-D-Xylose (9.53%). Ribose does not appear to occupy its predicted position in the sequence and this points to other affects besides conformational instabilities which are not obvious but which are effecting the course of the hydrogenolysis reaction

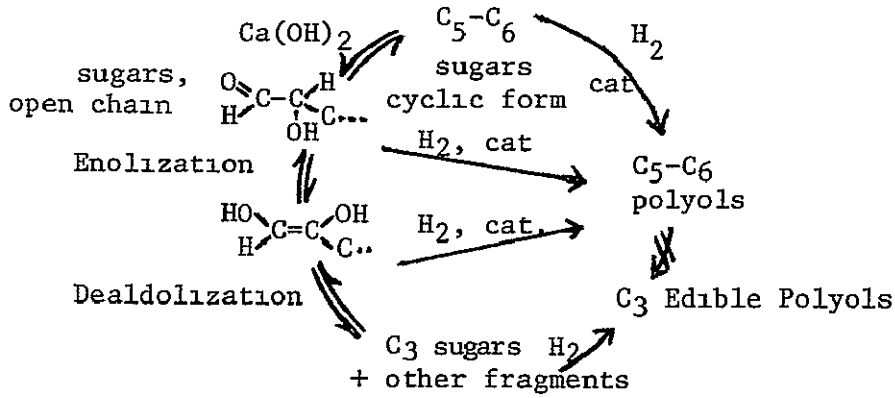
β-D-Xylose α-D-Xylose

Our results also show that the carbohydrate which yields the smallest amount of C_3 polyols does not necessarily produce the largest amount of C_5 or C_6 polyol Indeed that would be the case if hydrogenation of the starting material to yield high molecular weight polyols were the only reaction competing with the dealdolization process Pentitol production from C_5 sugars followed the sequence Arabinose (69 6%) > Ribose (34 5%) > Xylose (32.0%) while hexitol formation from both C_6 carbohydrates used followed the sequence Fructose (23%) > glucose (19.4%) In both cases, the order observed is not the one predicted from conformational considerations alone and other unapparent factors may well be affecting this complex reaction system It is apparent, however, that in every case studied, formation of high molecular weight polyols predominates over C_3 polyols production as shown in Table 7.

TABLE 7

Carbohydrate	Total C_3 Polyol Yield Wt %	Total C_5 or C_6 Polyol Yield Wt %
α-L-Arabinose	19 15	69 6
β-D-Ribose	4 39	34 5
β-D-Xylose	9.53	32 0
β-D-Fructose	20 24	23
β-D-Glucose	10 39	19 4

This can be explained by examining the following reaction scheme



While Pentitols and hexitols may form via direct hydrogenation of the cyclic structures of pentoses and hexoses, they certainly obtain as a result of hydrogenation of their open chain structures and the enediol formed after the enolization step All these reactions which are decreasing the pentose and hexose concentrations occur prior to triose formation and it is no wonder that pentitols and hexitols occur to a larger extent than triols Whether C_5-C_6 polyols result preferably from the hydrogenation of cyclic or open chain (or both) structure could not be determined Figure 10 shows the rate of hydrogenation of fructose in the absence of calcium hydroxide while Figure 9 shows the rate of hydrogen uptake by the same starting material in a reaction system where dealdolization is made to take place by the addition of calcium hydroxide In this latter case hydrogen consumption was slower because of the resulting depletion of C_6 sugars to C_3 (and other) carbohydrates via dealdolization These data are not sufficient to permit any kind of a conclusion concerning the predominating pathway for the hydrogenation of hexoses and pentoses

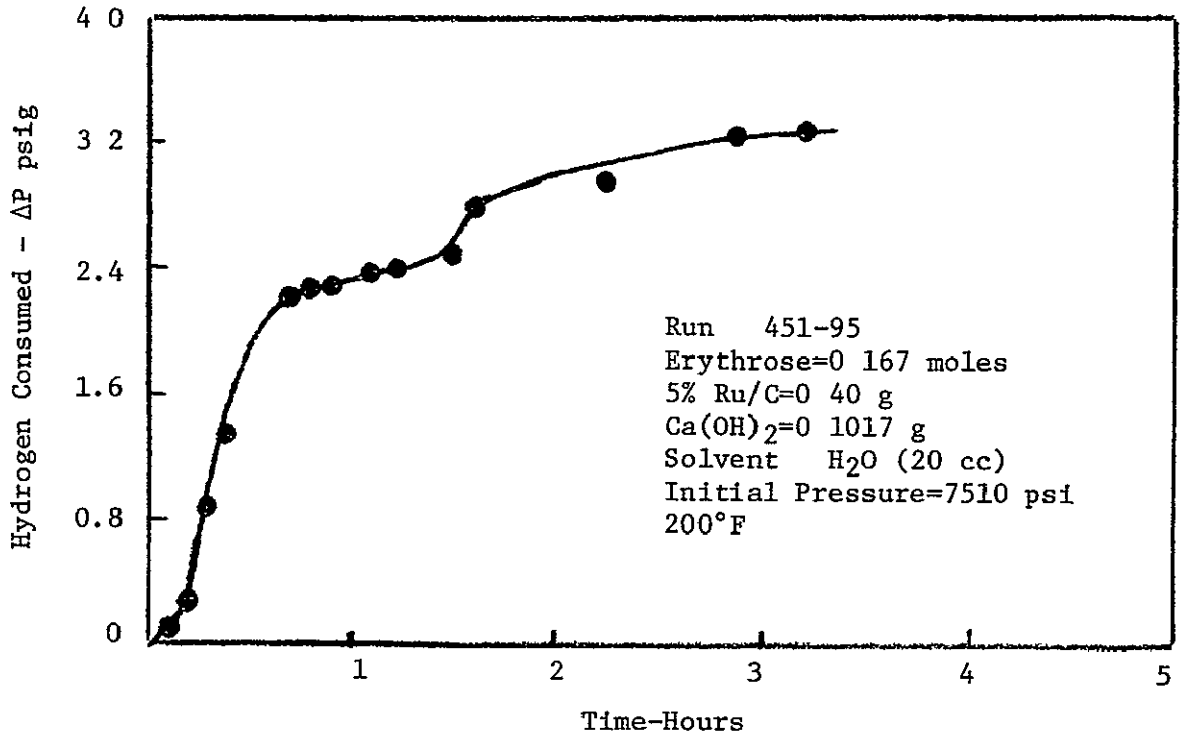
The hydrogenolysis of erythrose, another possible component of synthetic formose mixtures, was also investigated A very small amount of hydrogen was consumed by the C_4 sugar which yielded more ethylene glycol (3.34%) than glycerol (1 48%) The rest of the product mixture consisted of erythritol (7.62%) and starting material Material balance was lowest in this case and it is suspected that other reactions took place as evidenced by the change in slope of the hydrogen consumption curve (Figure 12) Such reactions might have led to the formation of relatively volatile products which might have been lost during the venting of the system or during the evaporation of the solvent

Finally, trioses were subjected to the hydrogenolysis reaction with the aim of determining whether, under the present experimental conditions, trioses yield C_3 polyols exclusively or whether they are lost (and to what extent) to other undesirable products The results were as follows Dihydroxyacetone yielded 38 73% polyols compared to 18 19% for glyceraldehyde Hexitols, products of triose dimerization followed by hydrogenation also formed to the extent of 2% and 12 7% for dihydroxyacetone and glyceraldehyde, respectively. Finally dealdolization of C_3 sugars followed by recombination and hydrogenation accounted for the formation of erytritols, pentitols and 1,2,4-butanetriol. The conclusion to be drawn from these data is that, even in the ideal case where cleavage of hexoses to trioses, for instance, occurs to the extent of 100%, at best still 60% of the C_3 sugars are converted into undesirable products

In conclusion, the results described in the foregoing discussion reveal that hydrogenation of C_5-C_6 carbohydrates (and other intermediates) occurs more readily than their conversion to C_3 polyols. These results also indicate that becaus

FIGURE 12

RATE OF HYDROGEN UPTAKE



of the presence of alkali (co-catalyst), trioses undergo aldol-reverse aldol condensation whose hydrogenation products are nutritionally undersirable This points conclusively to the need for a formulation of a catalyst(s) which will promote selective C_5-C_6 cleavage in the presence of hydrogen to C_3 polyols at the expense of C_5-C_6 sugar hydrogenation reaction and of aldolization-dealdolization of trioses

c Effect of Hydrogen Pressure

The effect of hydrogen pressure on glycerol and propylene glycol yield was studied for both fructose and glucose and Figures 13 and 14 very clearly show the correlation between hydrogen pressure and percent C_3 polyol For glucose, an increase in the yield of glycerol was first observed when the pressure was increased from 300 to 500 psig, under 1000 psig, however, the percent glycerol decreased sharply, indicating that at this pressure other competing processes, including the hydrogenation of starting material and other intermediates, have begun to take place, thus diminishing glycerol yield. The same argument applies to propylene glycol whose maximum production occurs under 300 psig hydrogen pressure and decreases thereafter as the initial hydrogen pressure is increased In the case of fructose, a similar though not as sharp an effect is observed. A marked increase in glycerol yield obtains as the pressure is increased from 75 psig to 500 psig, but remains somewhat insensitive to an additional increase in pressure to 1000 psig As to percent propylene glycol, it is observed to decrease at 1000 psig after it reaches its maximum at 500 psig. These results are conclusive in demonstrating the sensitivity of the hydrogenolysis system to initial hydrogen pressure The fact that C_3

Figure 13

Effect of H_2 Pressure on C_3 Polyol Yield

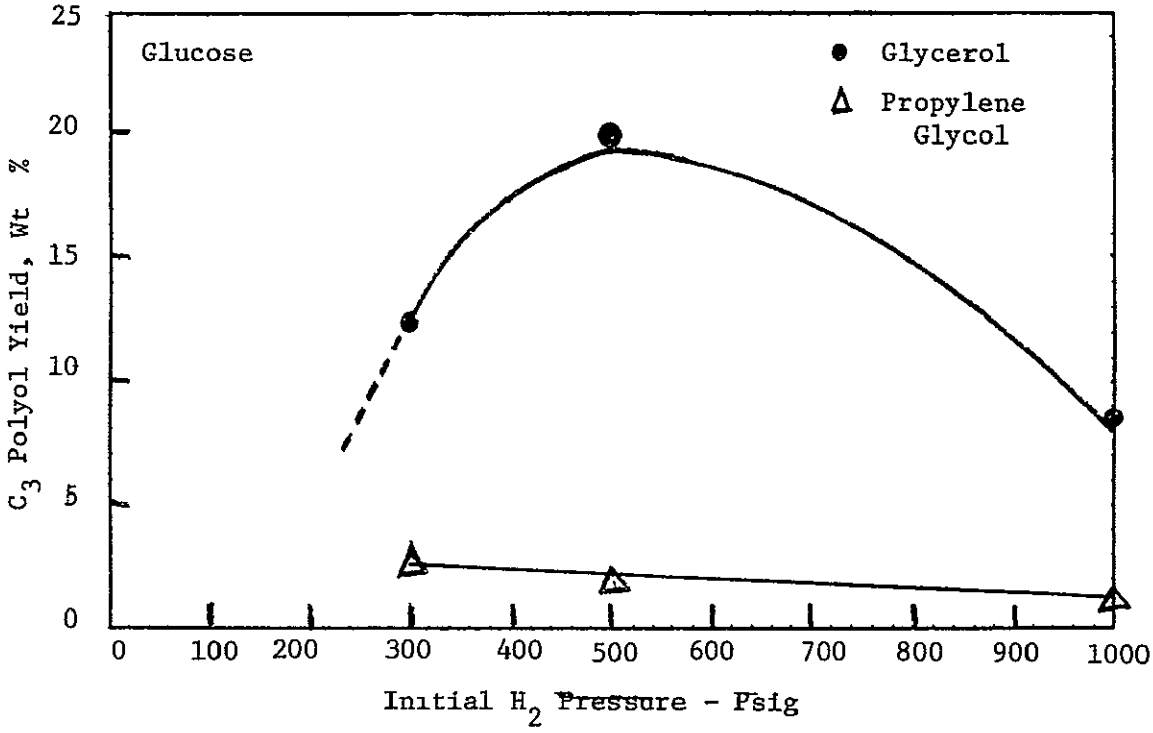
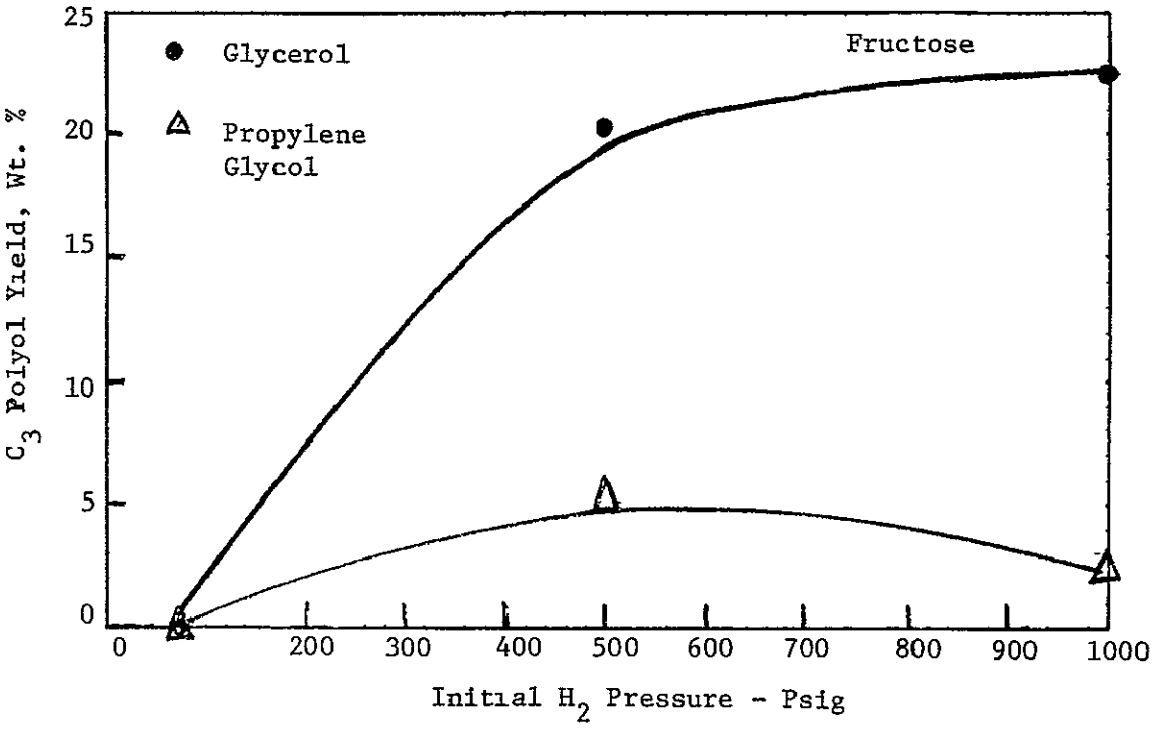


Figure 14

Effect of H_2 Pressure on C_3 Polyol Yield



polyol production diminishes or at best remains essentially constant when the pressure is increased from 500 psig to 1000 psig should be encouraging. Indeed for space application lower pressures will reduce power requirement and compressor weight However, as discussed in the previous section, utilization of new catalysts may change the pressure requirement completely, in which case trade-offs will have to be made. This, however, remains to be seen.

Figure 15

Rate of Hydrogen Uptake

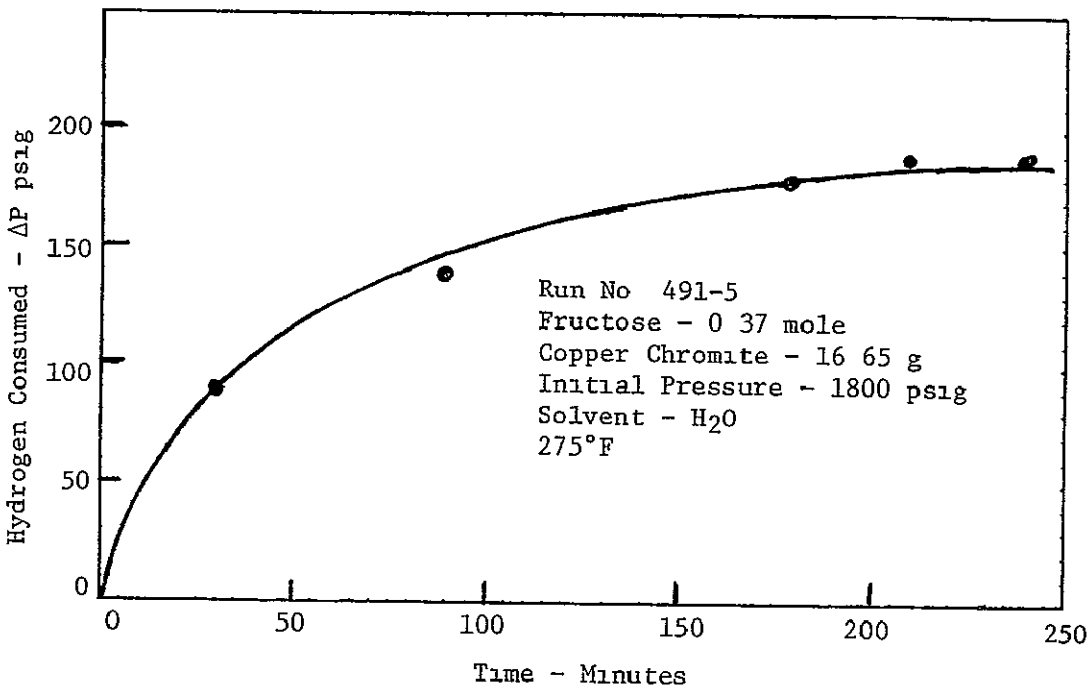


Figure 16

Rate of Hydrogen Uptake

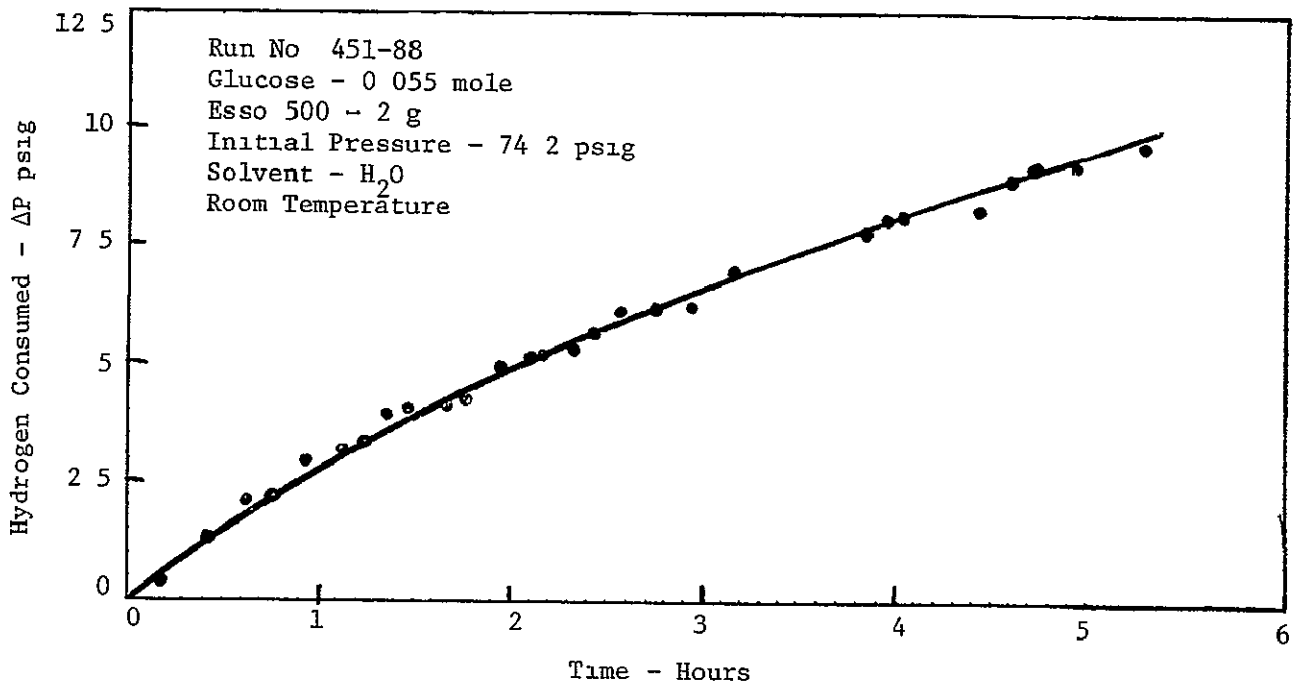


Figure 17

Rate of Hydrogen Uptake

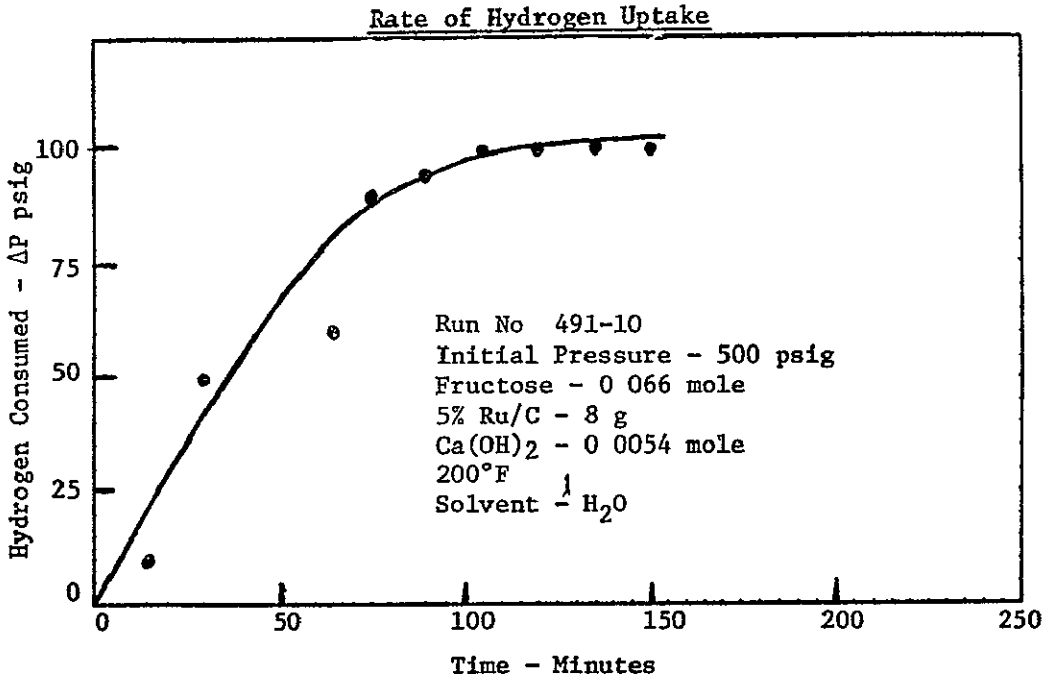


Figure 18

Rate of Hydrogen Uptake

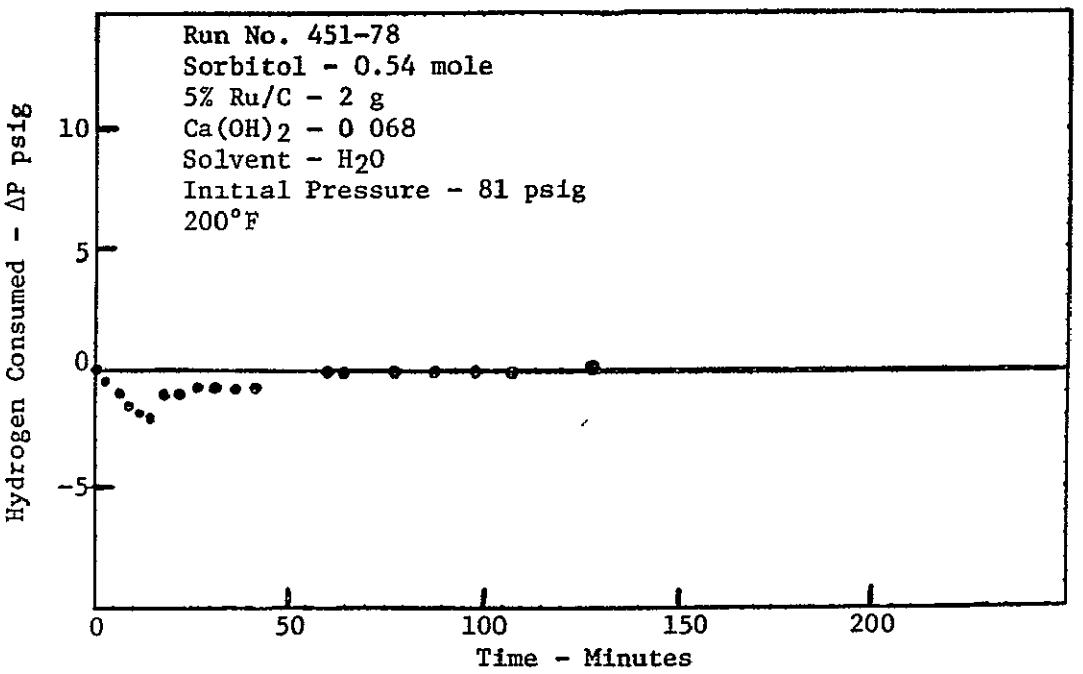


Figure 19

Rate of Hydrogen Uptake

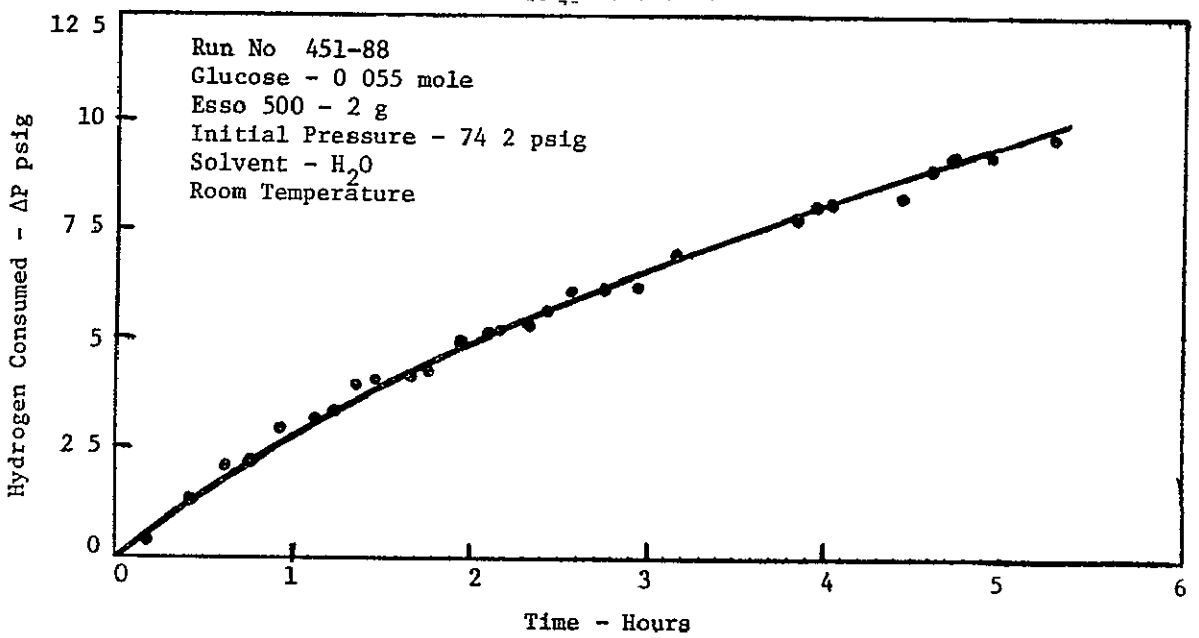


Figure 20

Rate of Hydrogen Uptake

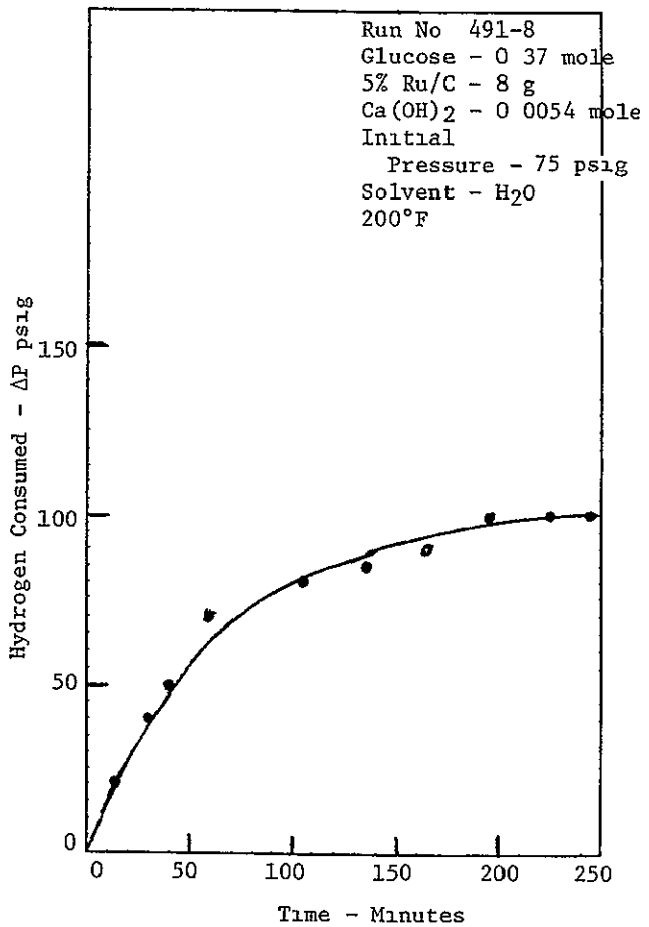


Figure 21

Rate of Hydrogen Uptake

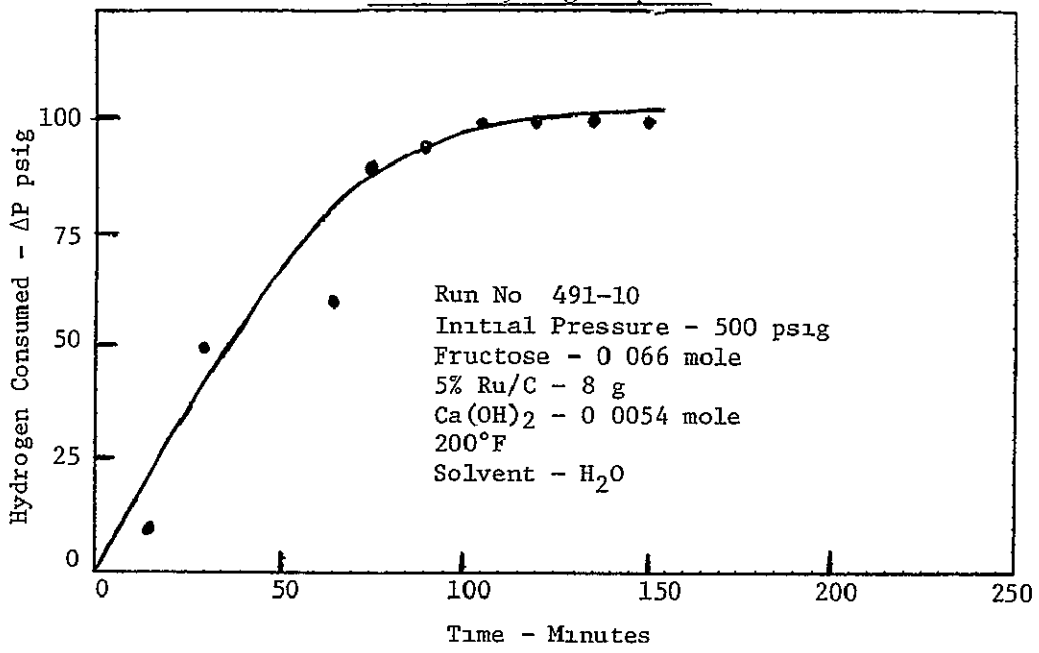


Figure 22

Rate of Hydrogen Uptake

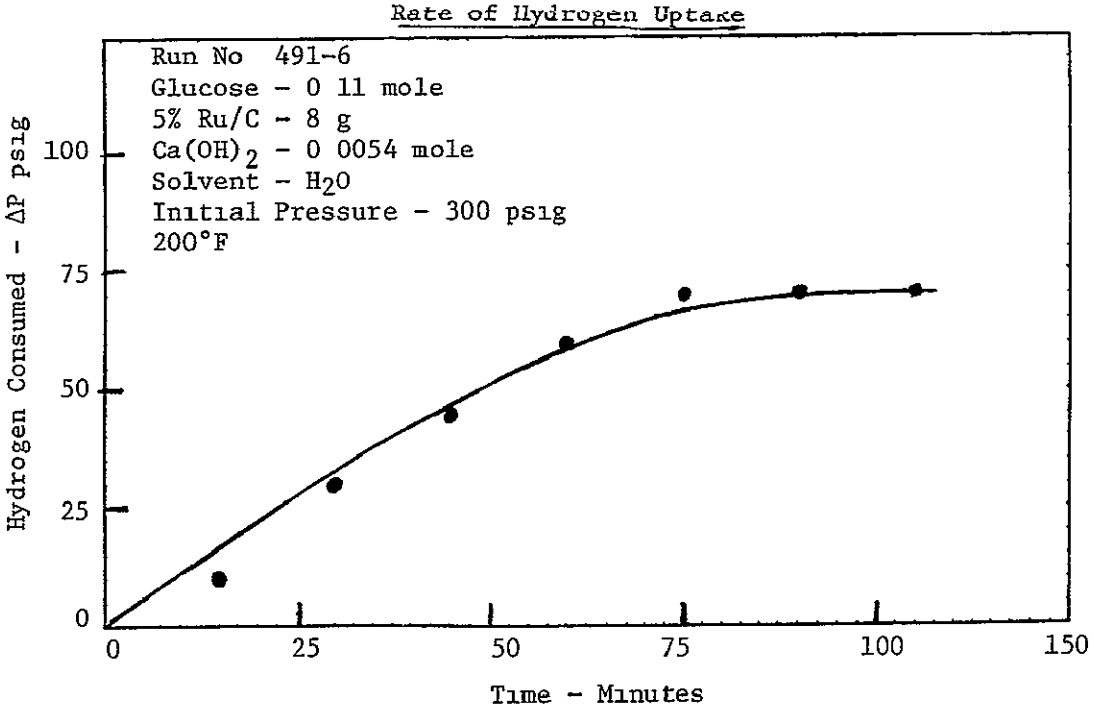


Figure 23

Rate of Hydrogen Uptake

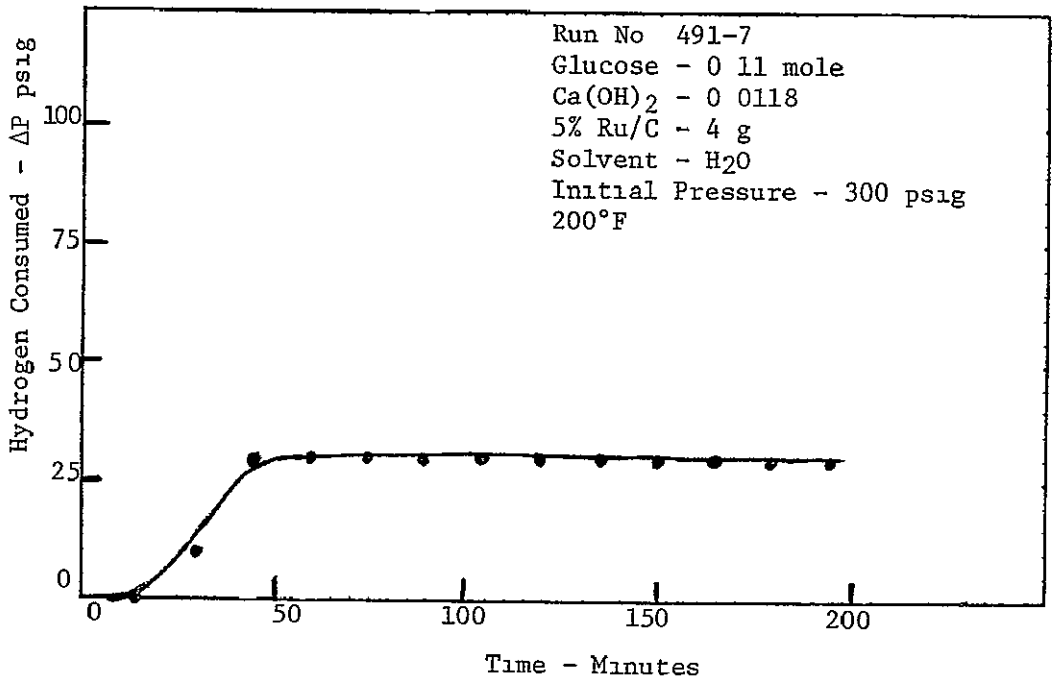


Figure 24

Rate of Hydrogen Uptake

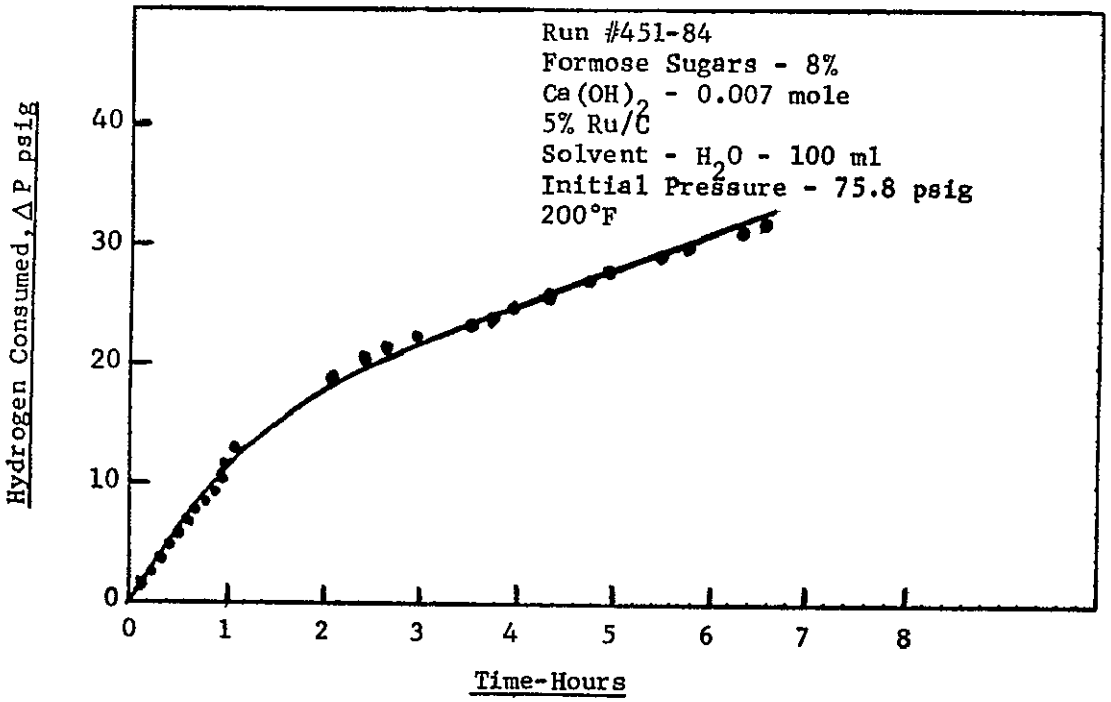


Figure 25

Rate of Hydrogen Uptake

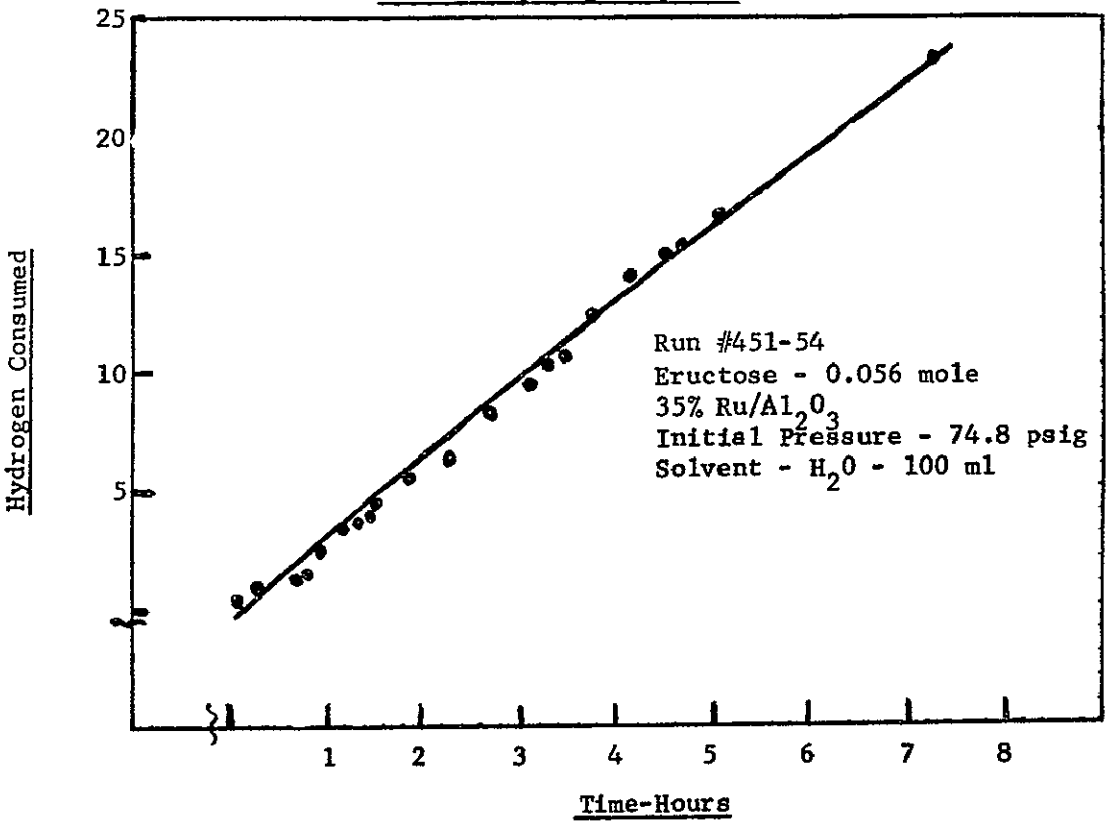


Figure 26

Rate of Hydrogen Uptake

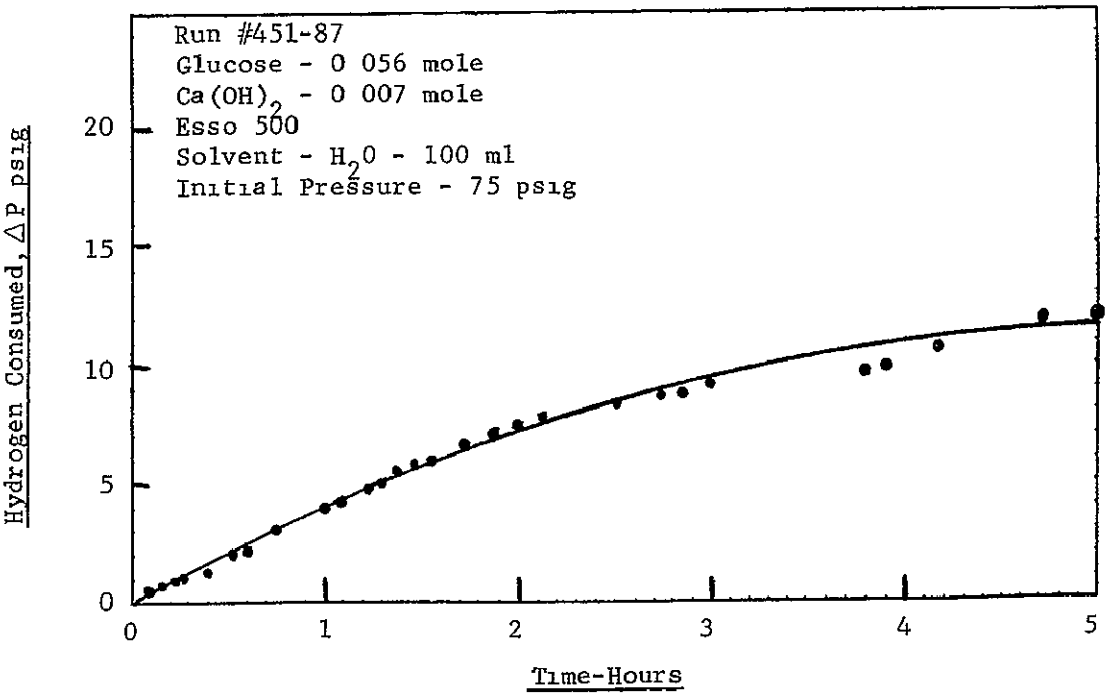


Figure 27

Rate of Hydrogen Uptake

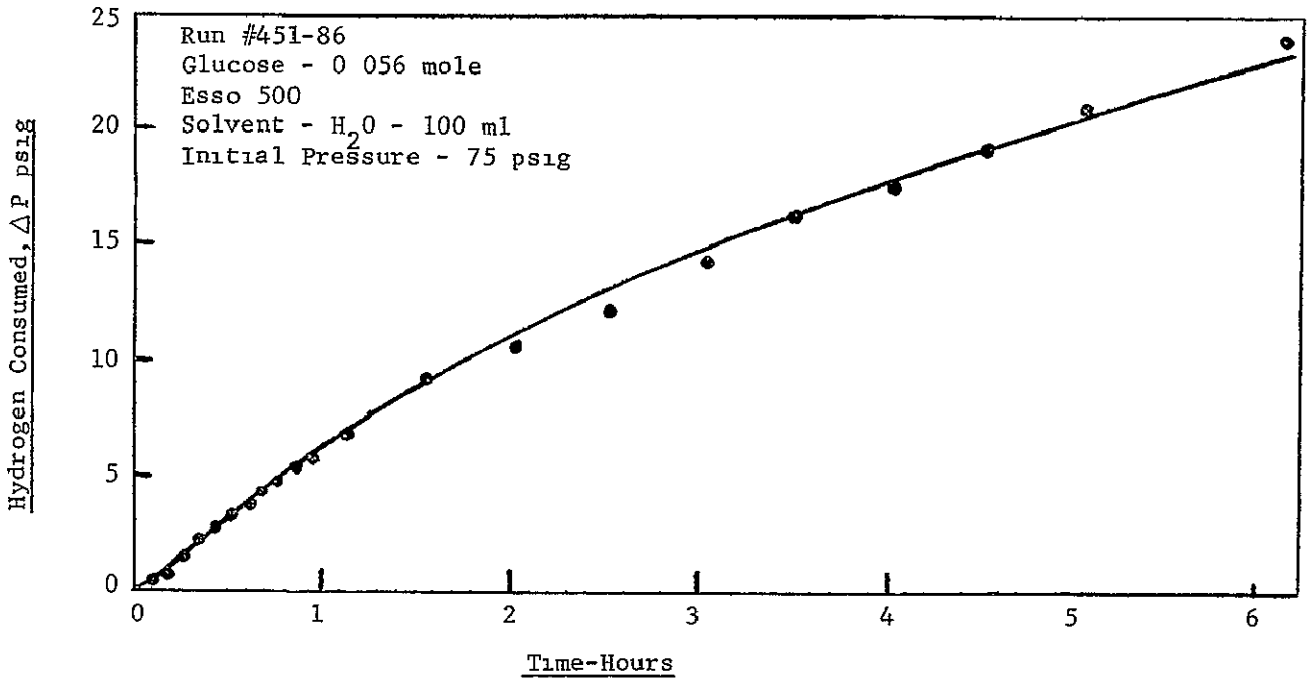


Figure 28

Rate of Hydrogen Uptake

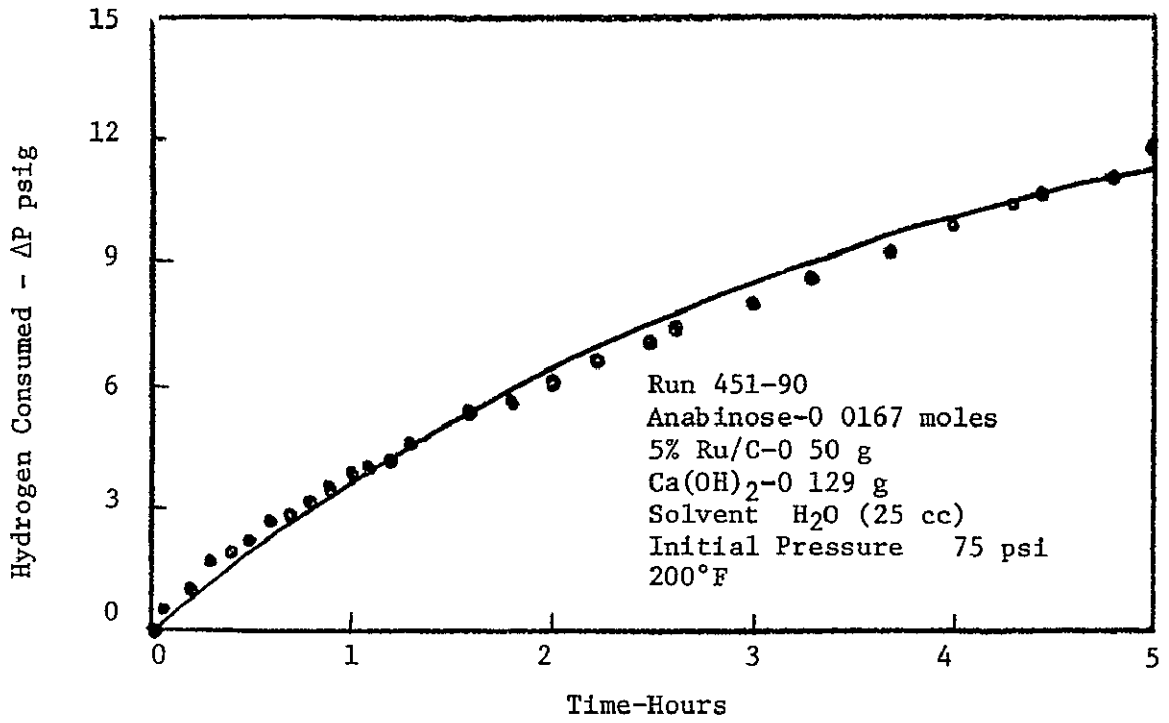


Figure 29

Rate of Hydrogen Uptake

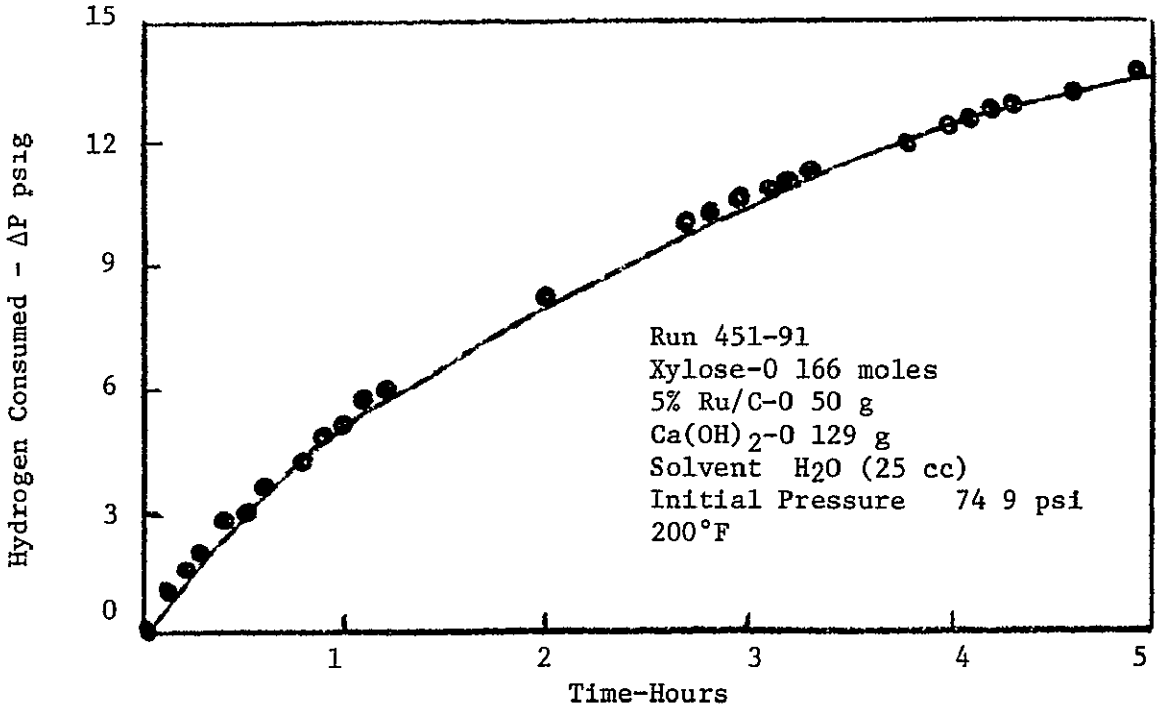


Figure 30

Rate of Hydrogen Uptake

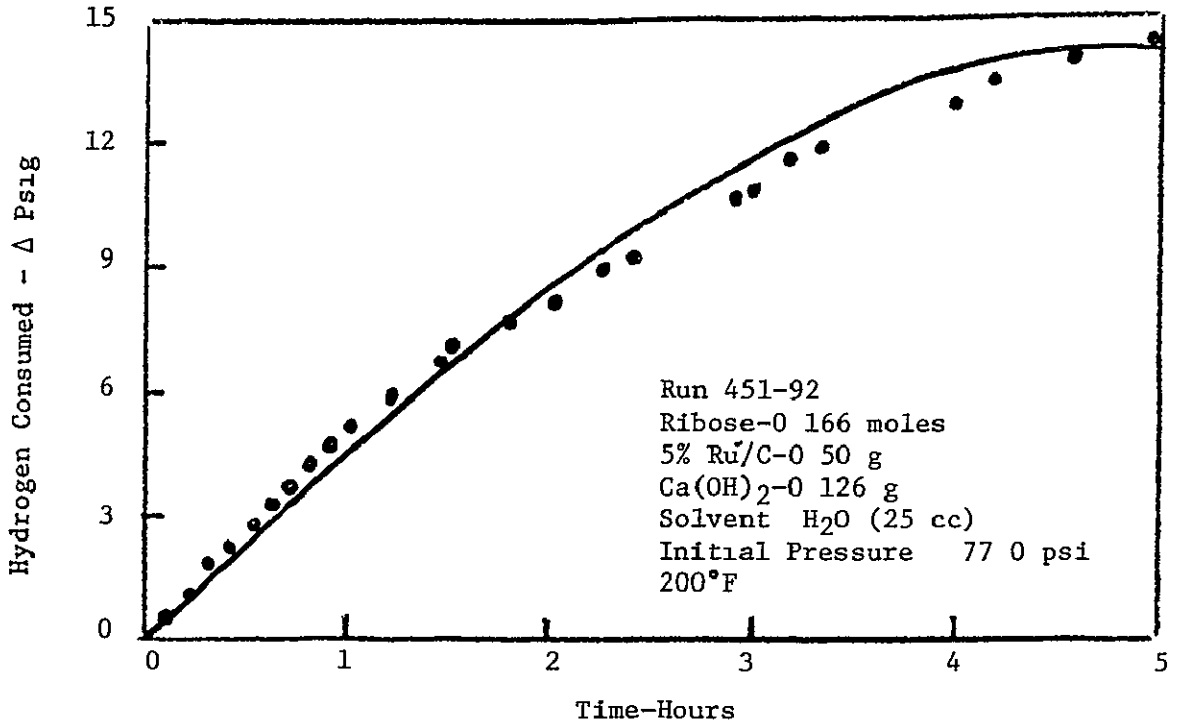


Figure 31

Rate of Hydrogen Uptake

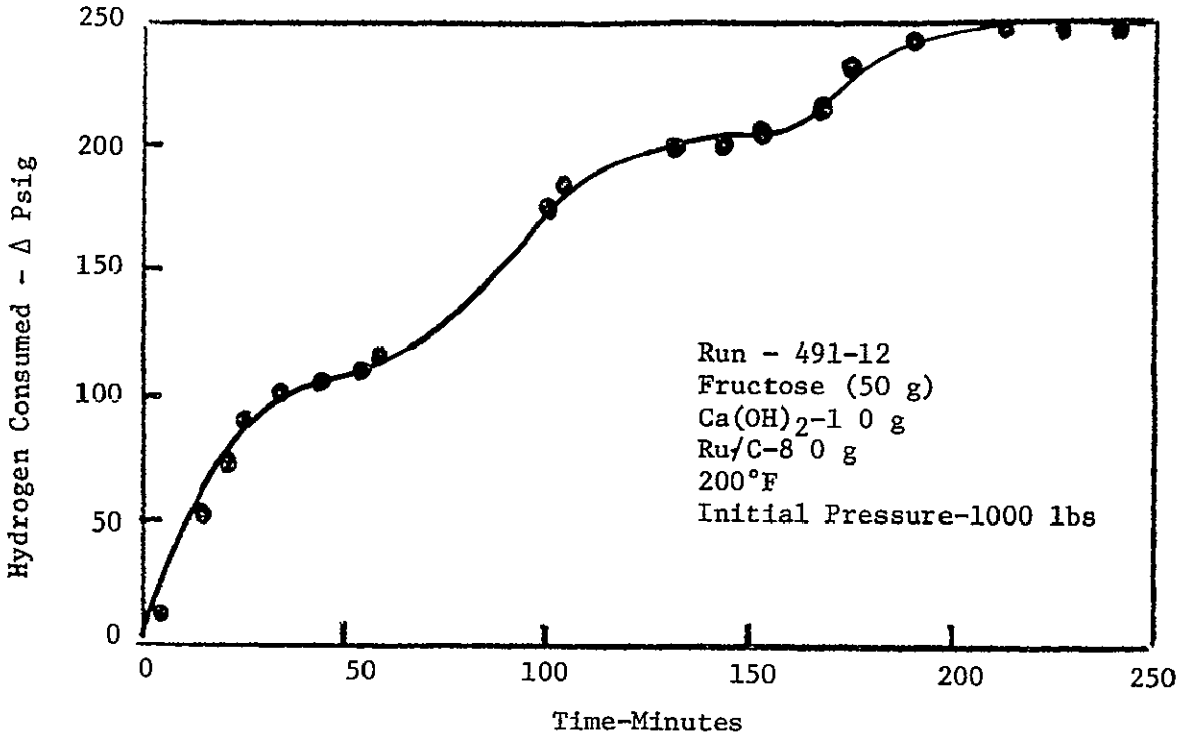


Figure 32

Rate of Hydrogen Uptake

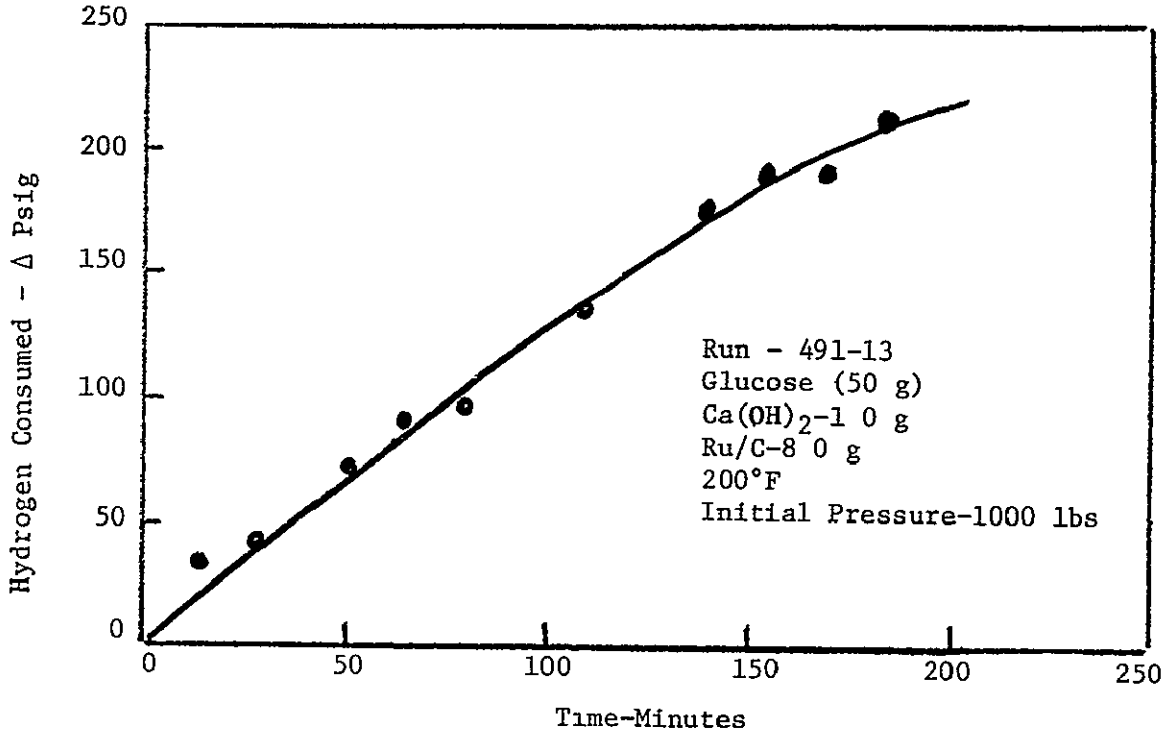


Figure 33

Rate of Hydrogen Uptake

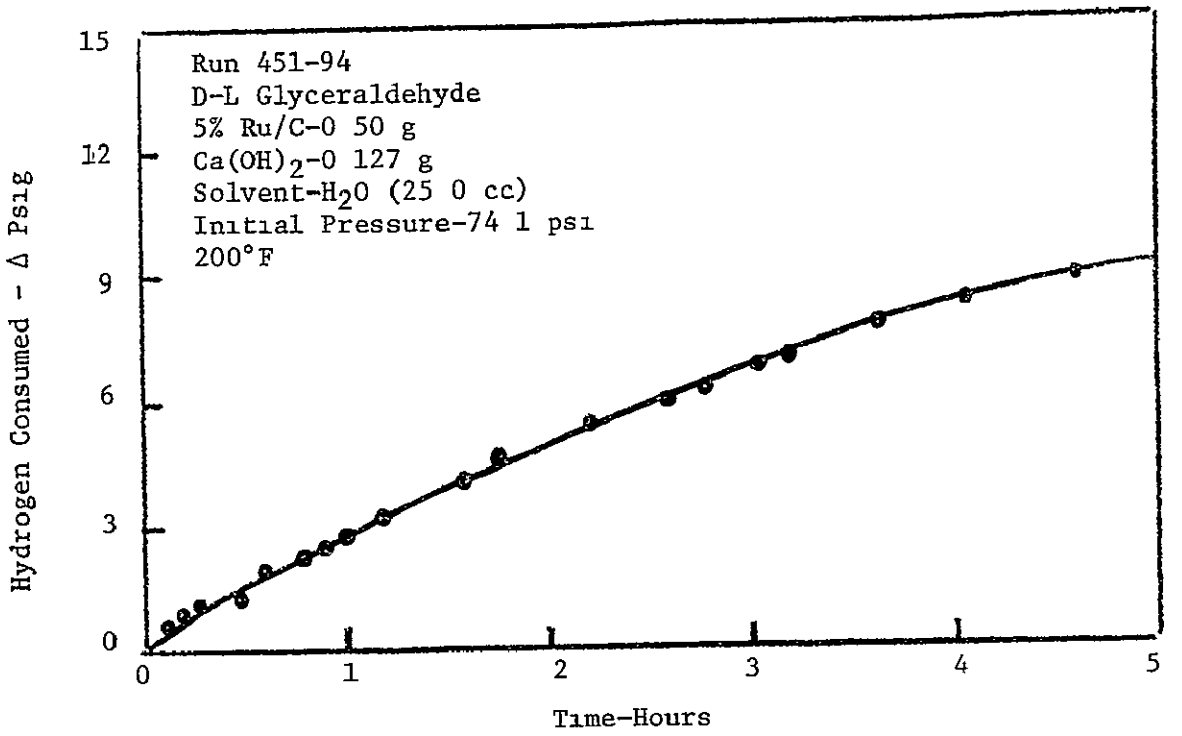
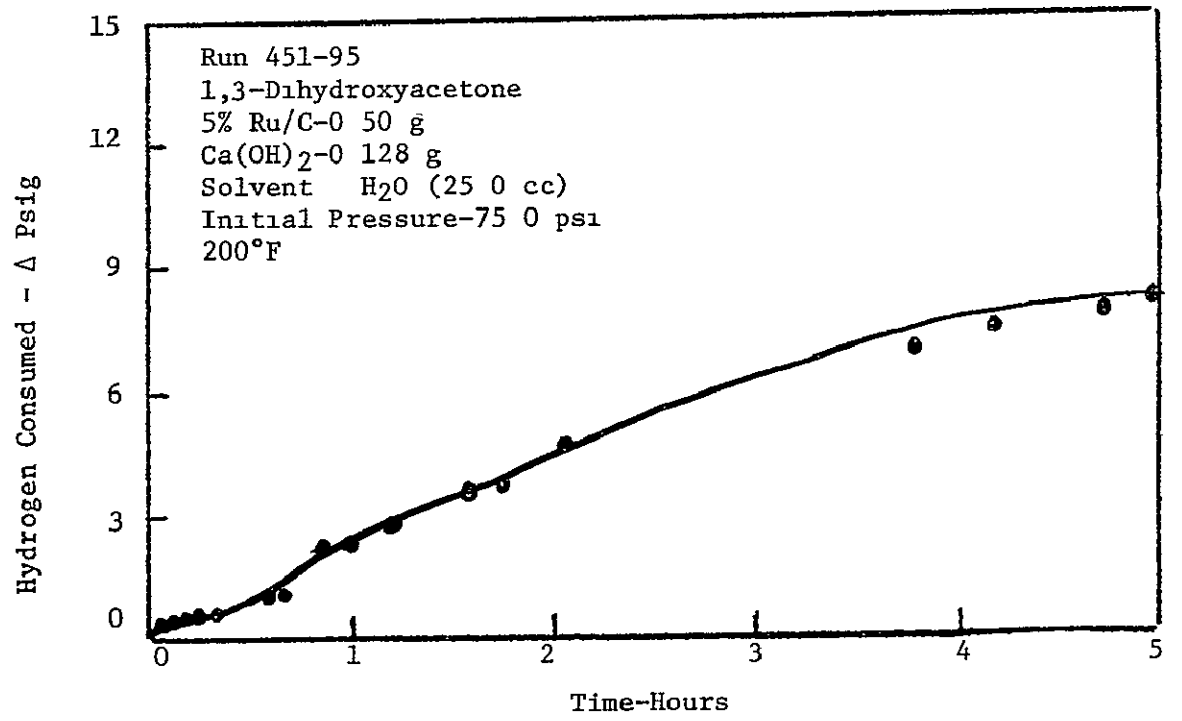


Figure 34

Rate of Hydrogen Uptake



2 Hydrogenolysis of Formose Feed Mixtures

With the aim of discovering a formose feed mixture which affords good yields of C_3 polyols, various synthetic sugar mixtures were prepared (Table 8) and subjected to hydrogenolysis Three of the mixtures tested were synthesized in the manner described by A Weiss and J Shapira (28) All formose mixtures were prepared in a batch reactor with the same mixing speed. The procedure involved heating the formaldehyde solution under nitrogen to the desired temperature at which time catalyst and co-catalyst are added and the reaction was begun. After the desired time elapsed, the mixture was cooled and calcium hydroxide precipitated as the oxalate salt A given volume of the formse mixture was transferred to the hydrogenolysis reactor (low pressure Parr hydrogenator or high pressure autoclave) where it underwent hydrogenolysis as described for neat carbohydrates Tables 9 and 10summarize the results obtained and the chromatograms of all runs attempted appear in Appendices 54-70. Also rates of hydrogen uptake for the same runs are shown in Figures 35-45

(a) Low Pressure Studies

In the generation of formose feed mixtures, residence time was varied so the feed which yields the largest amount of edible C_3 polyols can be identified Other formose feed mixtures, prepared according to the procedure of A Weiss (28) except for the use of glycolaldehyde as co-catalyst, were also tested so they too, could be evaluated as possible feed mixtures to use in the glycerol demonstration unit

TABLE 8

FORMOSE RUNS

Feed No	Formaldehyde Concentration-Mole/l	$Ca(OH)_2$ Concentration-Mole/l	Glycolaldehyde Concentration-x 10^2 Mole/l	Temp °C	Residence Time-Min	% Conversion*
451-109	2 67	0 162	0 15	60	6	60
451-105	2 67	0 162	0 15	60	8 1/2	100
451-106	2 67	0 162	0 15	60	10	100
451-108	2 67	0 162	0 15	60	12	100
451 111	0 83	0 198	0 15	60	4 71	100 (80)**
451-112	2 39	0 117	0 15	60	4 55	45 (62 5)**
451-114	0 95	0 187	0 15	60	4 20	100 (99 04)**

*Based on sodium sulfite titration for unreacted formaldehyde

**Reported conversion levels

Tables 8, 9 and 10 show that while formaldehyde conversion increases as the residence time is increased, total C_3 polyol production from these feed mixtures increases to a maximum and decreases thereafter No C_3 polyol was obtained from the hydrogenolysis of the formose feed obtained from Run No 451-109 The latter was obtained under the shortest residence time and contained 40% unreacted formaldehyde which is known (Quarterly Report #5, 1969) to poison the ruthenium catalyst and inhibit the hydrogenation process (Figure 35) The fact that the reaction mixture consumed hydrogen is not obvious It may be presumed that in the presence of alkali, degradation of formose sugars occurred under these conditions and that their degradation products consumed hydrogen without a need for a catalyst Also, such products may be so volatile as to be lost during the venting process or the solvent evaporation step Suffice it to say that such formose mixture as the one just described and which corresponds to 60% formaldehyde conversion is not suitable for use at low pressures to produce C_3 polyols With very little or no formaldehyde present, however, the situation is as shown in Figure 16 At very near or complete formaldehyde conversion, as in Run No. 451-105 (a duplicate run showed the presence of 0.5% formaldehyde), total C_3 and C_5-C_6 polyol yields were 2.43% and 11 66%, respectively These same yields increased as the residence time of the formaldehyde condensation reaction was increased from 8 1/2 to 10 minutes, namely 18 47% and 22 08%, respectively. However, if the residence time of the formose reaction were to increase to 12 minutes, a decrease to 5 77% in the C_3 polyol yield would result, whereas the higher polyol content would further increase to 27% This points clearly to the fact that, as the formaldehyde condensation is allowed to proceed much beyond the time required for 100%

Figure 35

Rate of Hydrogen Uptake

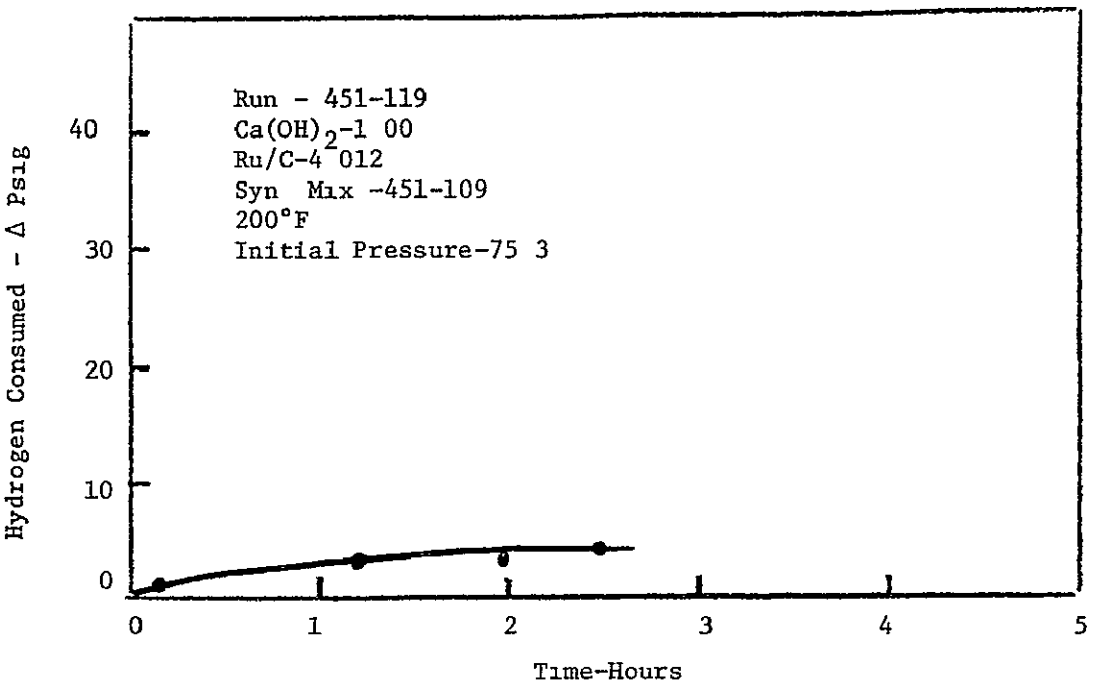
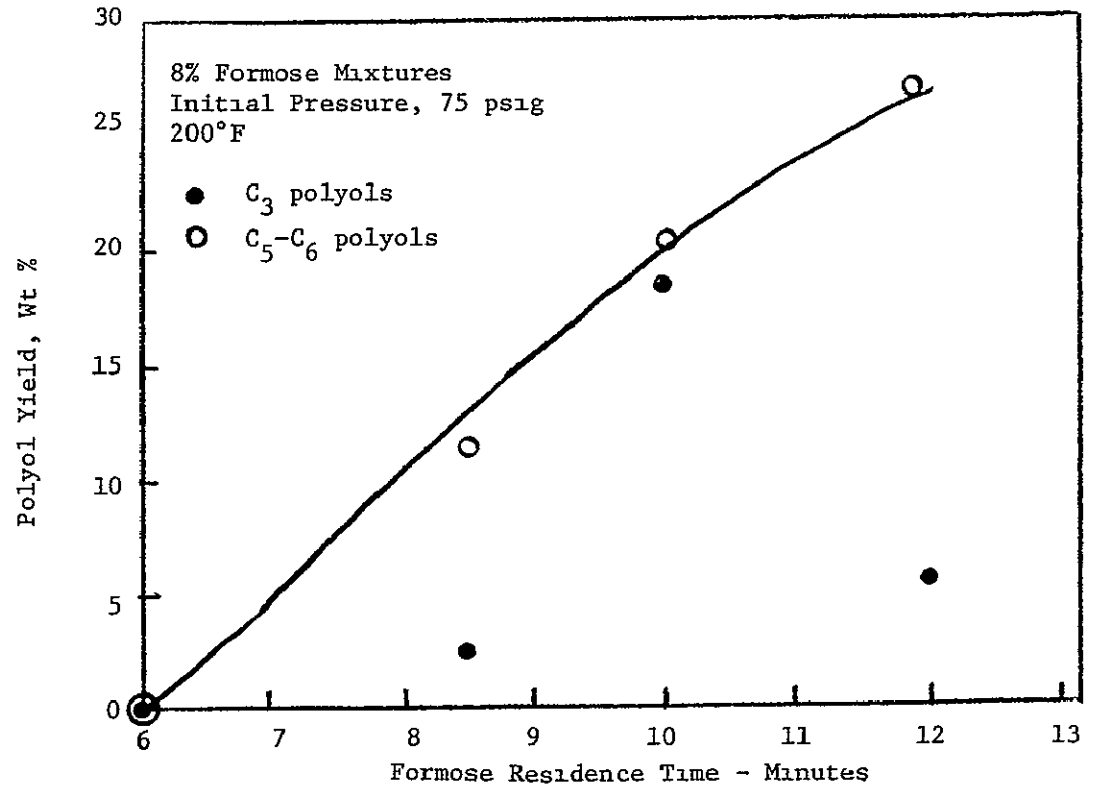


Figure 36

Relationship Between Polyol Yield and Residence Time of Formose Feed Mixture



conversion, undesirable products form which, upon hydrogenolysis, do not readily yield glycerol or propylene glycol

Hydrogenolysis of formose mixtures obtained using A Weiss' conditions led to the following observations. Those runs, such as No 451-112, which contained large amounts of unreacted formaldehyde, for the same reasons (catalsyt poisoning) mentioned above, did not yield any glycerol or propylene glycol Others, however, obtained at near or complete formaldehyde conversion did produce C_3 polyols though not to the same extent Run No 451-111 (100% formaldehyde conversion), for instance yielded, upon hydrogenolysis, 12 13% glycerol and propylene glycol while Run No 451-114 (99 7% formaldehyde conversion) yielded only 3 56% triols The observed difference, however, is a direct result of the different experimental conditions (see Table 8) used by the authors to generate the formose mixtures evaluated by us as potential sources for polyol production These differences in experimental conditions appear to significantly affect C_3 polyol yields and can be illustrated by comparing our own Run No 451-106 with A Weiss' No 451-111 The former yielded 18.47% C_3 polyols while the latter produced 12 13% of the sampe polyols. One feature common to all formose mixtures tested in this study is worth bringing to the surface, and that is C_5-C_6 polyol yield The latter is always observed to be larger than total C_3 polyol content This reveals a lack of selectivity of the hydrogenolysis reaction (under the present conditions) towards low molecular weight polyols and suggests that new hydrogenolysis catalysts might be needed

TABLE 9

HYDROGENOLYSIS OF FORMOSE FEED MIXTURES

Feed No	Amount of 5% Ru/C	$Ca(OH)_2$ Concentration-Mole/l	Temp °F	Initial Pressure, Psig	H_2 Uptake Psig	H_2 Uptake Moles	Theoretical* H_2 Uptake-Moles
451-109	4 00 g	0 135	200	75	11 3	0 0013	0 0888
451-105	4.00 g	0 135	200	75	46	0 0519	0 0888
451-106	4 00 g	0 135	200	75	40	0 0451	0 0888
451-108	4 00 g	0 135	200	75	22 9	0 0258	0 0888
451-111	4.00 g	0 135	200	75	40 3	0 0455	0 0927
451-112	4.00 g	0 135	200	75	16 2	0 0018	0 0796
451-114	4 00 g	0 135	200	75	21 6	0 0244	0 0316
451-109	8 00 g	0 054	200	1000	100	0 1699	0 222
451-106	8 00 g	0 054	200	500	55	0.0935	0 222
451-111	4.0 g	0 054	200	1000	85	0 154	0 1776

*Based on hydrogen uptake for complete hydrogenolysis, i e , 2 moles of H_2 per mole of carbohydrate, mixtures were assumed to consist entirely of C_6 carbohydrate

TABLE 10

HYDROGENOLYSIS OF FORMOSE FEED MIXTURES

Feed No	% Hydrogenolysis Conversion	Product Distribution - Wt %			
		Glycerol	Propylene Glycol	Ethylene Glycol	Other
451-109	14 35	--	--	--	--
451-105	58 45	2 09	2 33	5 87	C_4 polyol 9 60 C_5 polyol 6 51 C_6 polyol 5 15
451-106	50 79	17 0	1 47	4.75	C_4 polyol 4 5 C_5 polyol 19 26 C_6 polyol 2 82 butanetriol 6 10
451-108	29 05	5 77	0	0 53	C_4 polyol 6 51 C_5 polyol 18 37 C_6 polyol 10 37
451-111	49 95	10 39	1 74	4 13	Butanetriol 2 78 C_5 polyol 5 88 C_6 polyol 17.56
451-112	23 04	--	--	--	--
451-114	77 22	2 40	1 16	1 49	C_5 polyol 3 0
451-109	76 53	--	--	--	--
451-106	42 11	3 38	0	0 30	C_4 polyol 4 02 C_5 polyol 17 85 C_6 polyol 13 29
451-111	86 52	9 90	0	3 51	C_4 polyol 7 36 C_5 polyol 20 34 C_6 polyol 4 51

to correct the situation In evaluating the glycerol demonstration unit, therefore, close attention must be paid not only to the conditions under which the formose feed mixture is generated, but also to all parameters, and particularly to catalyst selectivity affecting C_3 polyol production.

(b) High Pressure Studies

In order to correlate the effect of hydrogen pressure with total yield of edible polyols, Runs No 451-109, 451-106, and 451-111 were hydrogenolyzed at 1000, 500 and 1000 psig, respectively It was hoped that these high pressures would keep the surface of the ruthenium on carbon relatively clean (especially in those cases where large amounts of unreacted formaldehyde are present as in Run No 451-109), thus improving C_3 polyol yields Unfortunately, this was not found to be the case (see Tables 9 and 10). Indeed, the catalyst poisoning effect of unreacted formaldehyde was still evident, as neither glycerol nor propylene glycol formed in the hydrogenolysis reaction of formose feed No 451-109 (containing 40% unreacted formaldehyde) Moreover, hydrogenation of C_5-C_6 carbohydrates (which would be expected to be pressure dependent) takes precedence over the hydrogenolysis process leading to a decrease in the yield of low molecular weight polyols and an increase in that of the C_6 polyols This can be readily observed for Runs No 451-106 and 451-111 (Tables 9 and 10) In the latter case, however, the small magnitude of these changes could again be traced back to the conditions under which the particular formose feed mixture was generated In any event, these directional effects of hydrogen pressure on total C_3 polyol yields are in agreement with those observed for the hydrogenolysis reaction of neat pentoses and hexoses and which were discussed earlier in this report From these data, it appears,

therefore, that higher hydrogen pressures will not be required to affect hydrogenolysis of synthetic sugar mixtures under the present experimental conditions (200°F, 5% Ru/Cas catalyst and $Ca(OH)_2$ as co-catalyst) On the other hand, since other catalysts may be needed to improve the currently low selectivity of the process to C_3 polyols, the pressure requirement may turn out to be altogether different. Hopefully, it will fall within a practical range for spacecraft application

Figure 37

Rate of Hydrogen Uptake

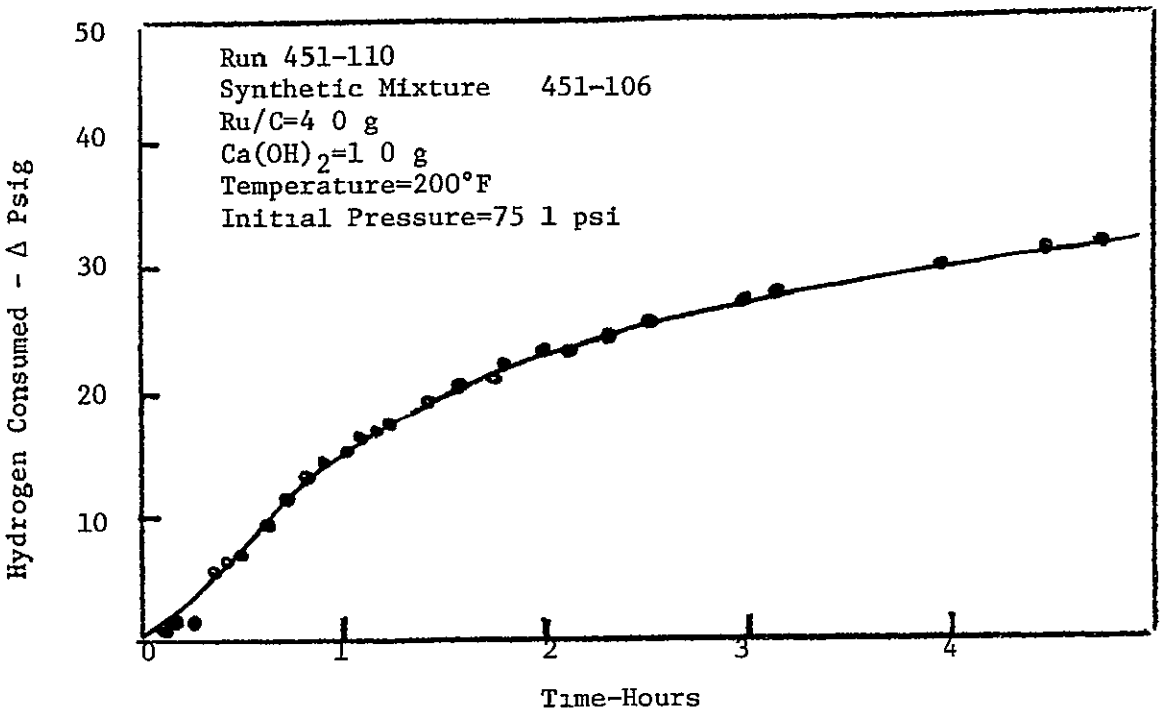


Figure 38

Rate of Hydrogen Uptake

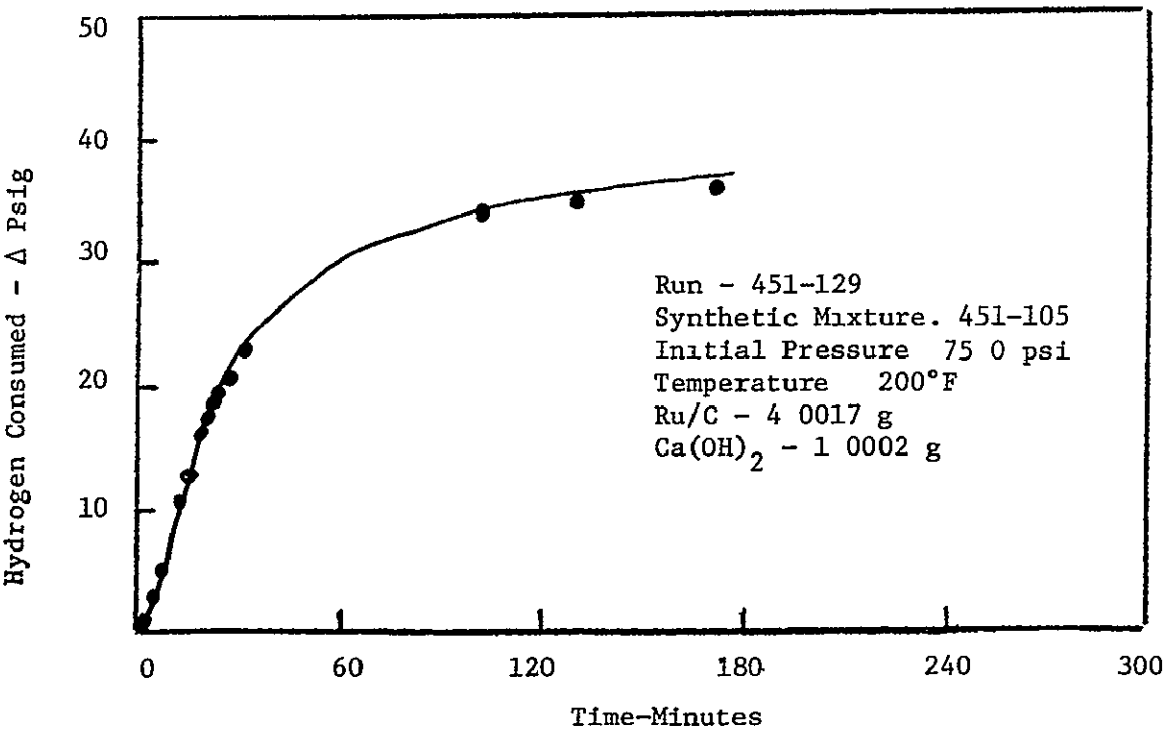


Figure 39

Rate of Hydrogen Uptake

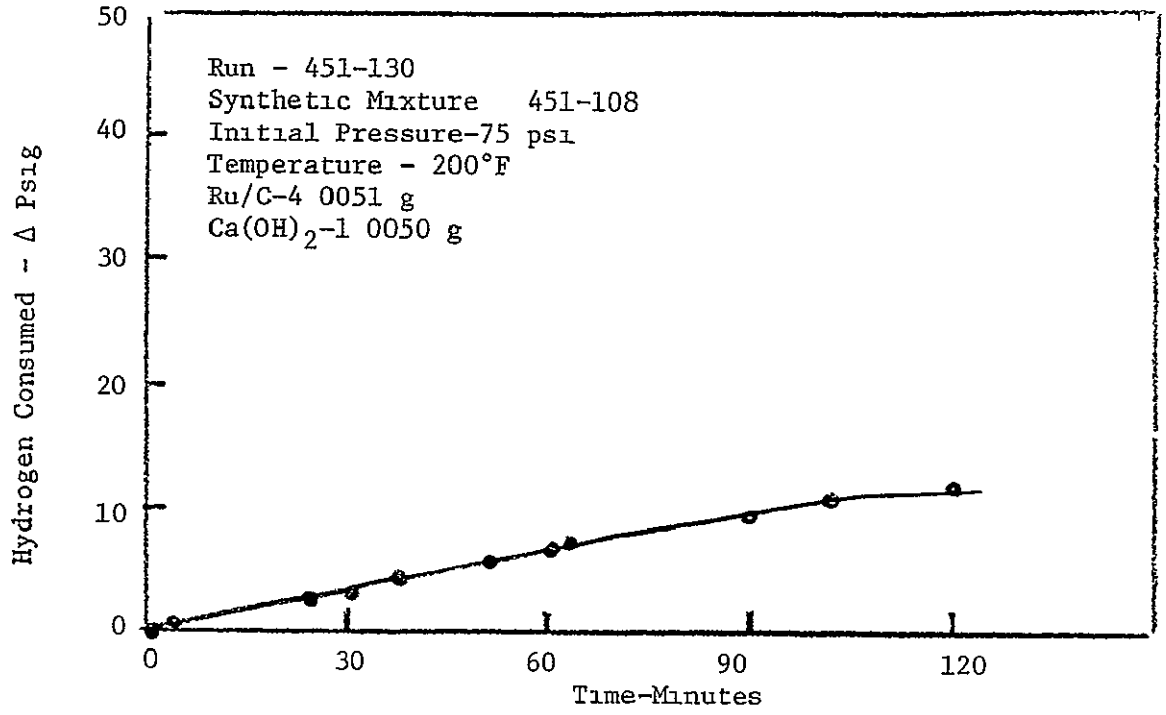


Figure 40

Rate of Hydrogen Uptake

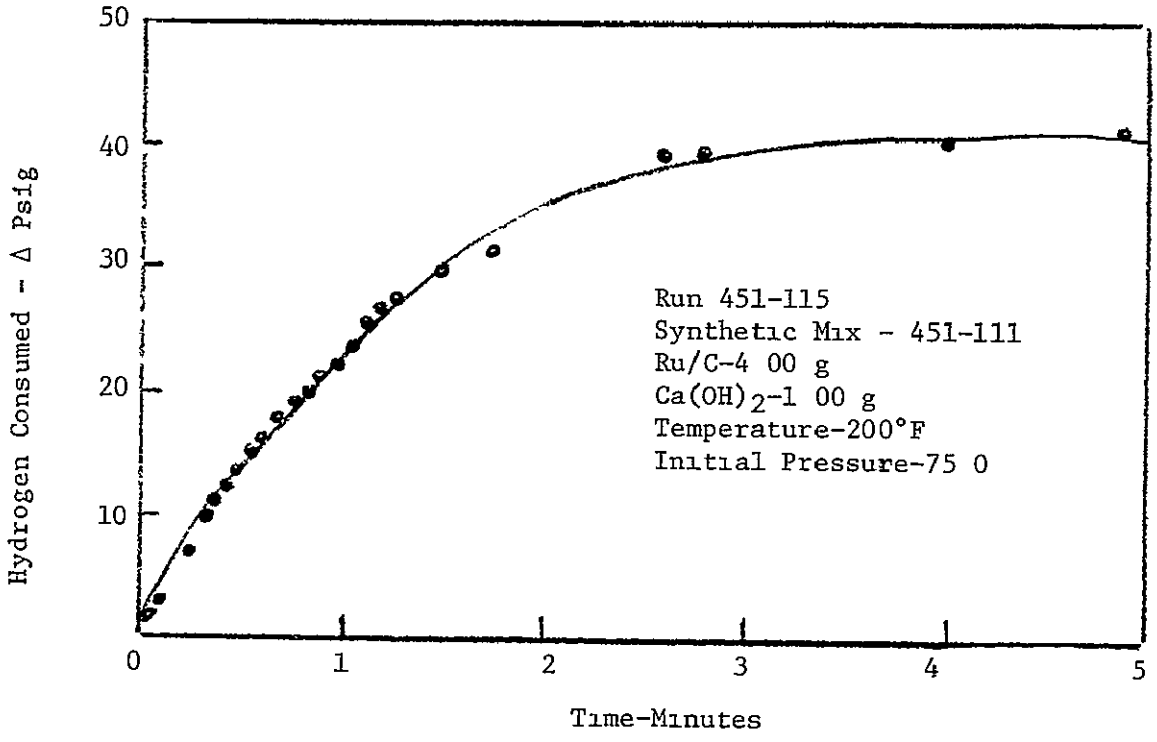


Figure 41

Rate of Hydrogen Uptake

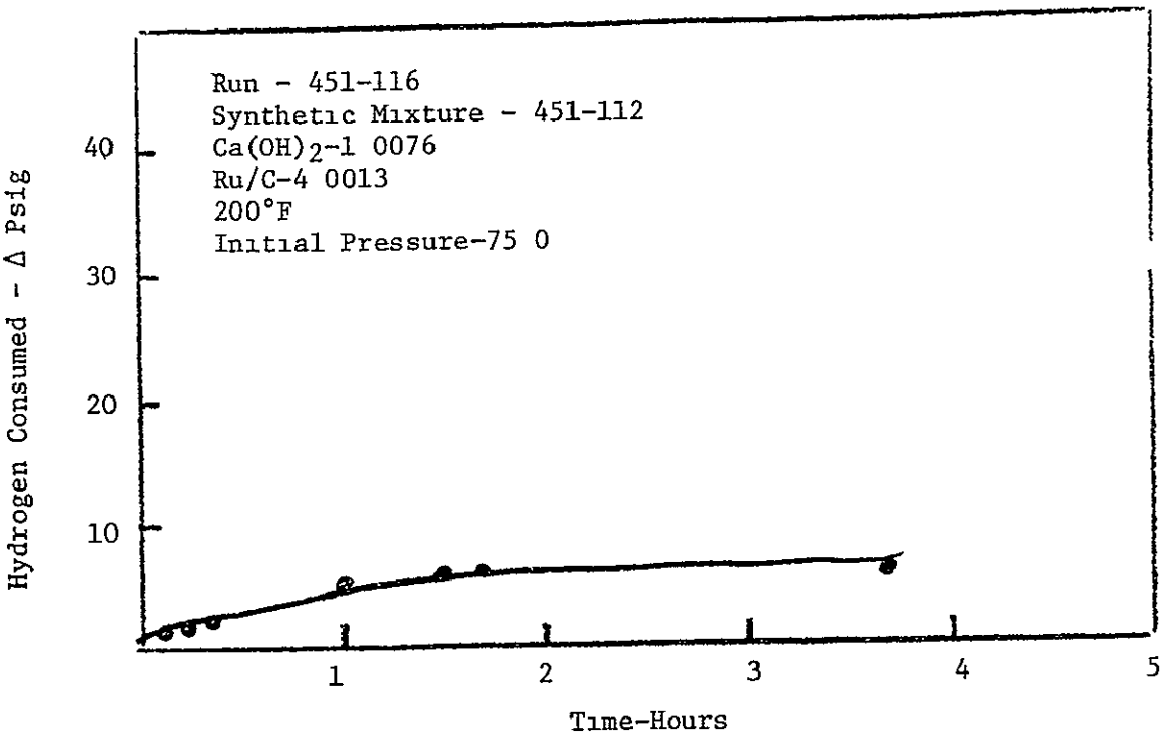


Figure 42

Rate of Hydrogen Uptake

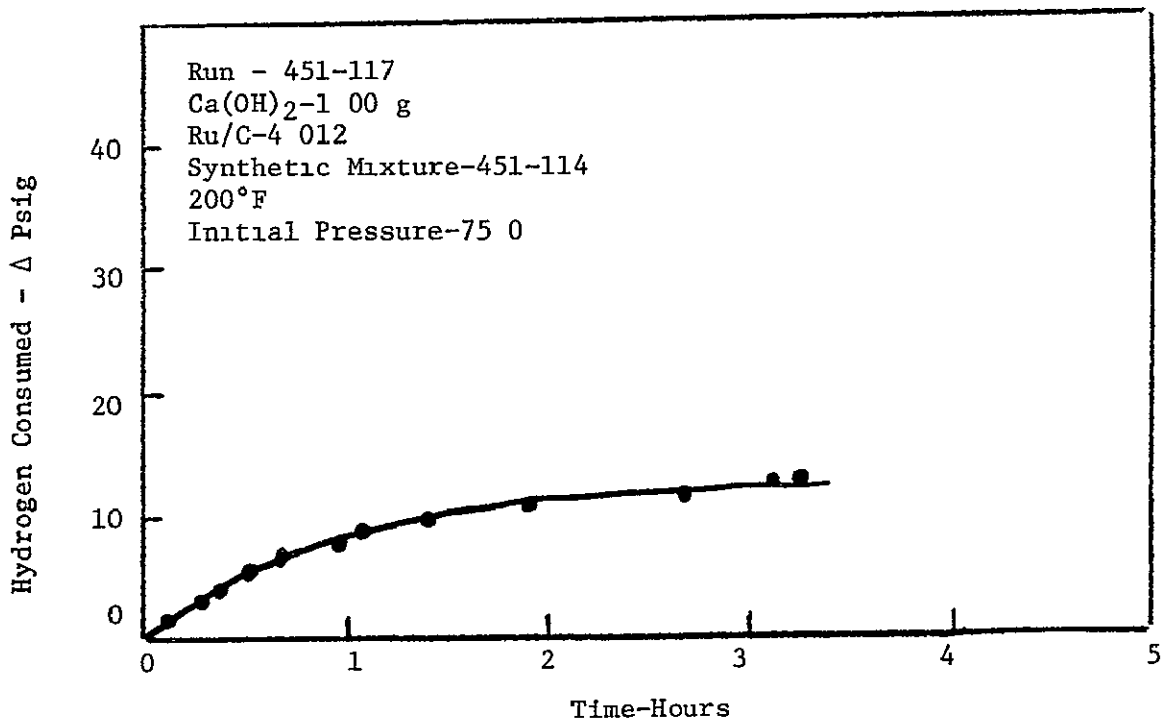


Figure 43

Rate of Hydrogen Uptake

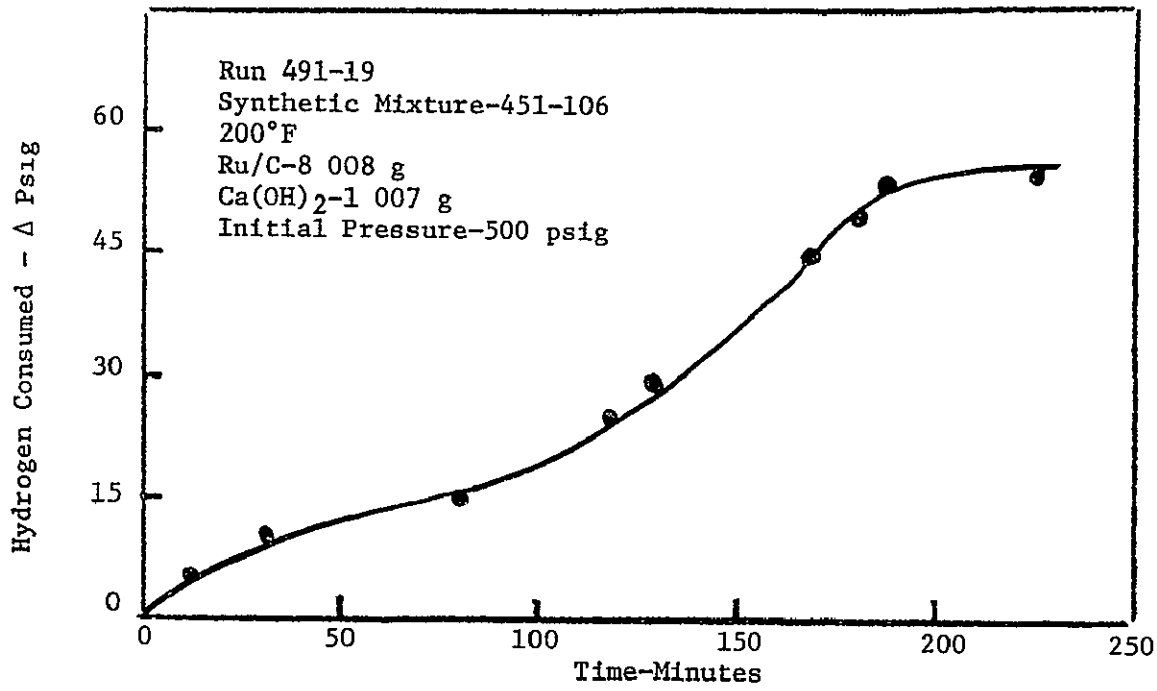


Figure 44

Rate of Hydrogen Uptake

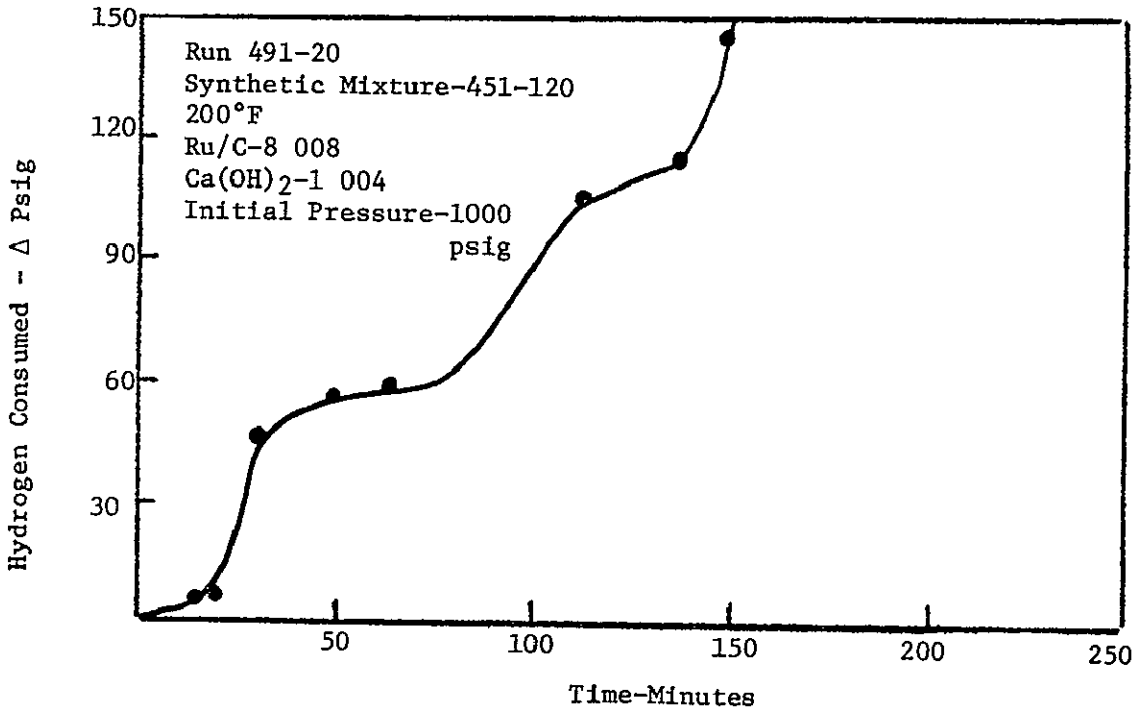
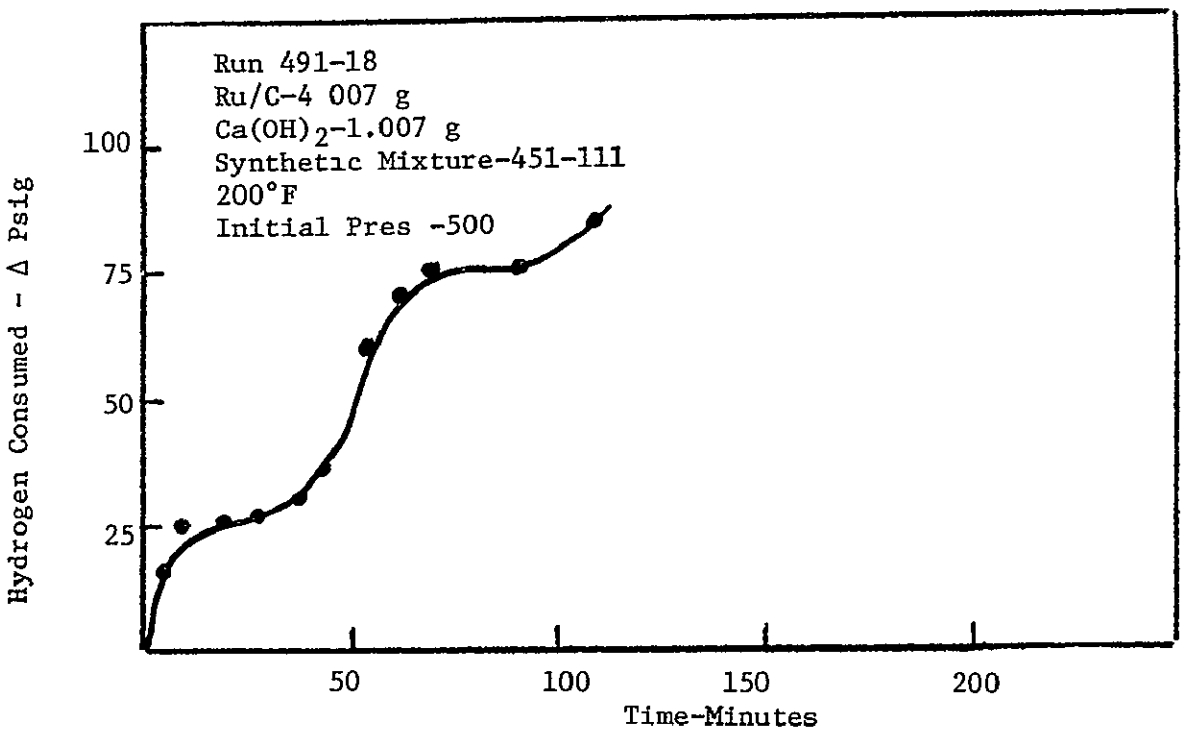


Figure 45

Rate of Hydrogen Uptake



D Polyol Separation Studies

In order for the polyol producing process to be practical, the products obtained therefrom must be readily separable from one another so purification of the desirable edible polyols will be possible Thus, two product mixtures resulting from the hydrogenolysis of formose feed No 451-106 were combined to yield a total weight of 5 64 g The results of the attempted separation of glycerol from the polyol mixture via vacuum distillation were as follows

Fraction No	Vapor Temp °C	Pressure mm Hg	Amount-g	Appearance	n_D^{20}
1	15-25	0 05	0 482	Colorless liquid	1 3548
2	25-90	0 50	0 8246	Colorless liquid	1.3974
3	90-110	0 50	1 3254	Yellow liquid	1 4514
Residue	--	0 50	--	Dark brown	--

An infrared spectrum of the first fraction showed it to consist predominantly of water A small amount of the glycols and 1,2,3-butanetriol was also shown to be present in this cut and may account for the observed high index of refraction A gas chromatographic analysis of the second fraction revealed the predominance in this cut of the glycols over water Finally glycerol was the main component of the third fraction as shown by gas-liquid chromatography However, several contaminants appeared to be present in this cut (see gas chromatogram, Appendix 71) among which were ethylene glycol, 1,2-propylene glycols and other higher boiling components An infrared spectrum of this third fraction further revealed the presence

of a carbonyl containing substance The latter was shown not to be dihydroxyacetone The C_3 sugar was mixed with glycerol and the mixture distilled under the same conditions as the one just described Only water and glycerol were collected, the triose caramelized in the still

In order to obtain a purer sample of glycerol, fraction #3 was redistilled in the same manner as described above The glycols were successfully separated from the glycerol and the higher boiling components Unfortunately, the inefficiency of the system and the small amount of sample prevented any further purification of the glycerol. We will, however, continue our efforts in this area so that pure glycerol will be obtained and data provided in order that the distillation section of the demonstration unit be designed

E Catalyst Fabrication

The design of the hydrogenolysis reactor requires that the catalyst be employed in the form of pellets This tends to avoid high pressure drops which lead to channeling and gas compression Using impregnation techniques, we are now preparing carbon supported ruthenium based catalysts in pellet form for use in the high pressure reactor Co-catalysts containing $Ca(OH)_2$ or CaO are also being prepared using the same technique The oxide, however, will be supported on alumina while the base will be supported on carbon Largely as a result of the use of catalyst in the form of large particles, diffusion into the catalyst particles may limit the hydrogenolysis reaction. Should the preliminary data prove this to be the case, the diffusion characteristics of the catalyst will be improved by adding a diffusion promoter

F Analytical Technique

Because they lack both volatility and thermal stability, sugars as such are not easily suited for gas chromatographic analysis Derivatization can and does afford sugar derivatives with sufficient volatility to allow their separation via gas-liquid chromatography One such method consists in identifying sugars via their trimethylsilyl derivatives (29) Individual sugar derivatives, however, produce more than one peak and, based on our experience, the method was found not to be straightforward A better method is the one in which sugars and polyols are identified as the trifluoroacetyl derivatives (30,31).

Using the internal standard method (16), we obtained area factors for carbohydrates and polyols trifluoroacetyl derivatives which are shown in Tables 11 and 12 respectively, as well as the program temperatures at which individual derivatives appear This method affords two major improvements over Sweeley's technique It eliminates duplicity of peaks for individual derivatives and permits the observation of a linear relationship between peak area and concentration of the derivative under investigation Figures 46 and 47 show such a relationship for a mixture of polyols (ethylene glycol, glycerol, arabitol and sorbitol) and carbohydrates (arabinose and fructose), respectively Furthermore, mixtures of derivatives obtained via this method produce the same chromatogram after 48 hours as they do when they are freshly prepared The only drawback of the method is that C_6 carbohydrate and C_6 polyol derivatives, when present together, give rise to a broad peak whose individual components cannot be identified with certainty This occurs in the carbohydrate hydrogenolysis area where sugars and polyols are present in the reaction mixture However, since the glycerol and propylene glycol yield is the quantity of interest in this case, the merits of the method still stand All standard chromatograms are shown in Appendices 72-87

Table 11

Carbohydrate	Program Temperature °C	Relative Retention time* Min at 10°/min	Area Factor* mg/Unit Area
Glycolaldehyde[a]	66,90	0 61, 1 28	2 92
Glyceraldehyde[b]	129	2 38	1 25
1,3-Dihydroxyacetone[b]	121	2 15	2 76
Erythrose	98?	1 51	--
Xylose	100	1 56	0 66
Ribose	110	1 84	1 80
Arabinose	101	1 59	1 06
Glucose	115	1 98	0 88
Fructose	118	2 07	1 03
Galactose	114	1 96	1 36
Mannose[c]	115,119	1 98, 2 10	--
Glucoheptose	118	2 07	0 885

(a) Appears mostly as the dimer, the monomer peak is very weak

(b) Appears as the dimer

(c) Gives rise to two peaks

* Relative to glycerol

Table 12

Polyol	Program Temperature °C	Relative Retention Time* Min at 10°/min	Area Factor* mg/Unit Area
Ethylene Glycol	55-56	0 16	0 81
1,3-Propylene Glycol	68	0 32	0 59
1,2-Propylene Glycol	60	0 21	0 71
Glycerol	80	0 48	1 13
Erythritol	91	0 63	0 65
1,2,4-Butanediol	95	0 69	0 68
2,3-Butanediol	59	0 19	0 72
Adonitol	102	0 78	2 6
Xylitol	105	0 82	2 8
Arabitol	104	0 81	0 91
Sorbitol	119	1 01	1 18
Mannitol	111	0 90	0 80
Dulcitol	115	0 96	1 10

* Relative to glucoheptose

** Relative to glucoheptose which was used as the internal standard except for Sorbitol, Mannitol, and Dulcitol whose area factors were obtained relative to glycerol

Figure 46

Relationship Between Polyol Concentration and Detector Response

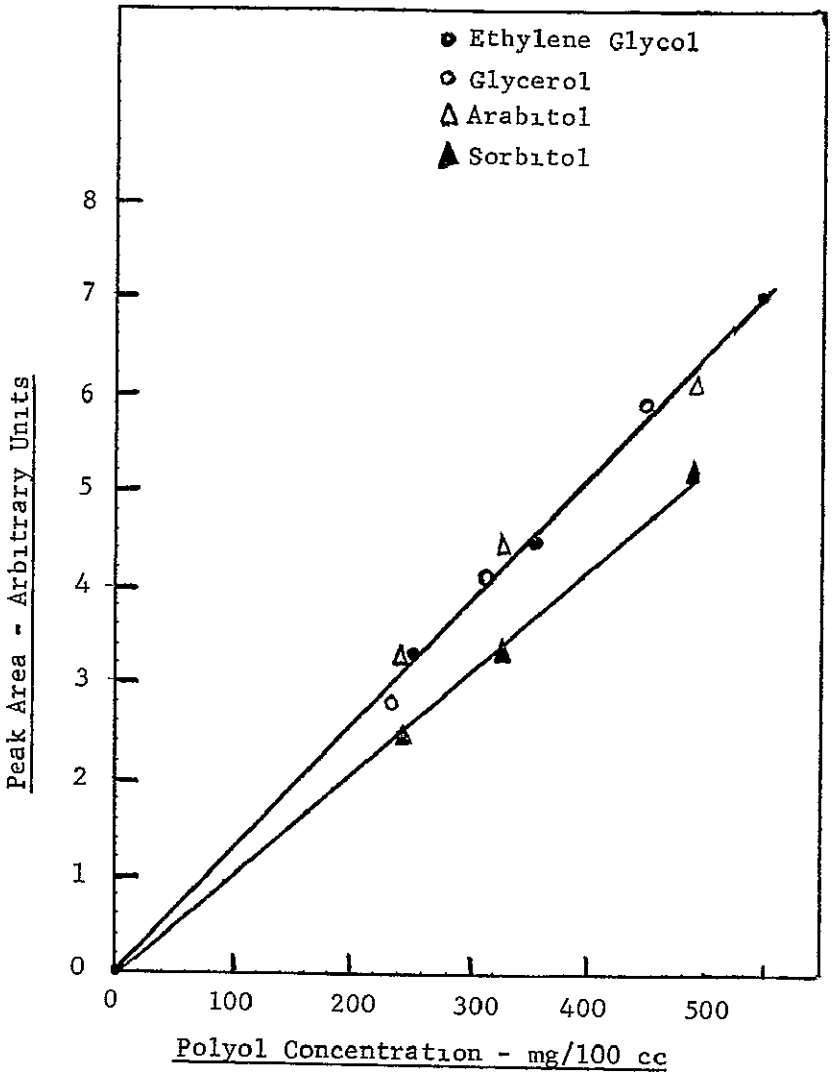
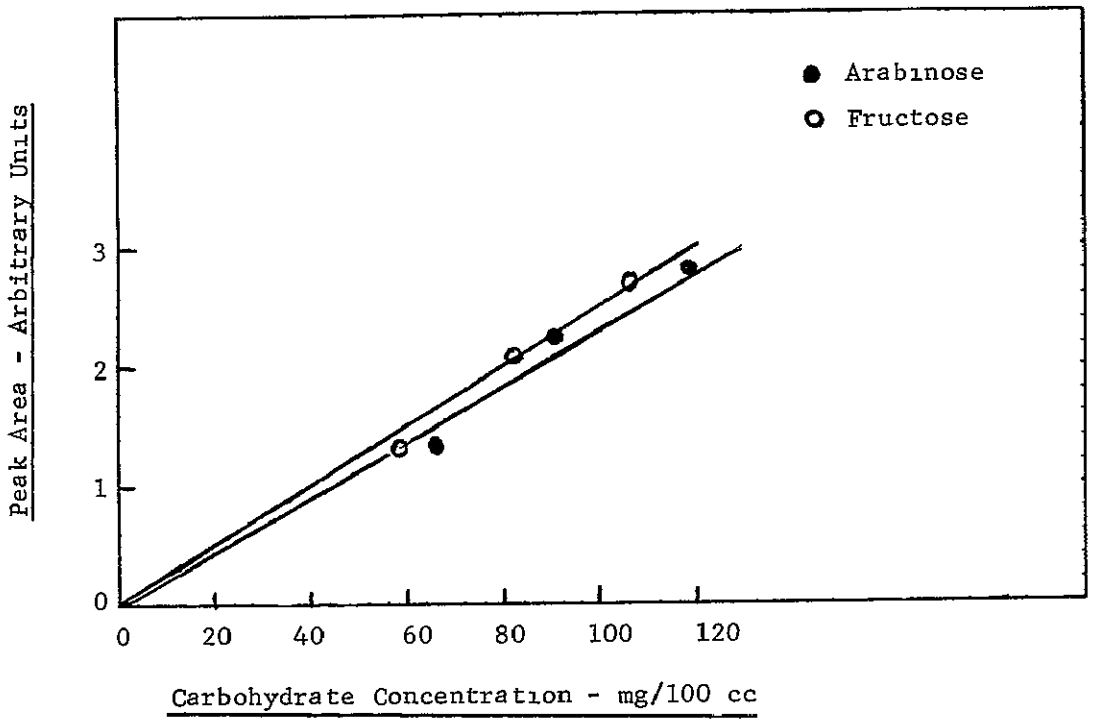


Figure 47

Relationship Between Carbohydrate Concentration and Detector Response



V. EXPERIMENTAL

Low pressure hydrogenolysis reactions were run as follows the desired amount of the carbohydrate or polyol was dissolved in 100 cc of distilled water and introduced into the hydrogenation flask, after which the catalyst (and where applicable the co-catalyst, i e , calcium hydroxide) was added The flask was then integrated in the Parr hydrogenation apparatus and the system pressured with hydrogen and vented three times Pressurization of the system to the desired reaction pressure (75 psig) was accomplished and the heat was turned on Hydrogen uptake was followed by recording the pressure drop as a function of time When the pressure ceased dropping or when the hydrogen uptake tapered off, the reaction was stopped, vented, cooled and the catalyst filtered When calcium hydroxide was used as co-catalyst, it was precipitated as the oxalate salt and filtered Following solvent evaporation under vacuum, the total product mixture was weighed and a sample was taken for GLC analysis High pressure hydrogenolysis reactions were run in essentially the same manner in a one-liter autoclave equipped with an air driven stirrer and a thermocouple

In the formaldehyde condensation reaction studies, experiments were run in the following manner 100 ml of 8% aqueous formaldehyde solution or as described by Weiss (obtained by diluting 37-40% commercial formalin solution) were heated under nitrogen until the temperature had reached 60°C. The proper amounts of catalyst and co-catalyst were then added and the reaction begun. After the desired reaction time had elapsed, the system was opened and the stoichiometric amount of oxalic acid added The mixture was then stirred for several minutes in an ice bath after which it was filtered The

precipitated calcium oxalate was dried and weighed and the filtrate passed through a column containing 20 g of each cation and anion exchange resins A weighed sample was taken at this point and titrated for unreacted formaldehyde using the sodium sulfite method (32), 100 cc or 250 cc of this solution were taken and used as a feed for the low and high pressure hydrogenolysis reaction, respectively Where this was not applicable, the remainder of the filtrate was concentrated under vacuum on a rotary evaporator after which the total product was weighed and a sample was taken for GLC analysis The latter was performed as follows To a weighed sample approximately 10-20 mg (formose or hydrogenolysis product) was added 1 cc of derivatizing solution (obtained by mixing 2 g of sodium trifluoroacetate with 20 ml of acetonitrile and 20 ml of trifluoroacetic anhydride) and the total mixture warmed at 35°C for 2 hours Ten to twenty microliters were then analyzed using the internal standard method (16) Use was made of a Barber Coleman model 5003 equipped with a flame ionization detector A U-shaped 6' x 1/4" stainless steel column packed with 3% SE-30 on Chromosorb W (80-100 mesh) was used under the following conditions The GC was run isothermally at 55°C for the first minute (Time Zero is the solvent front) after which the column temperature was programmed at 10°C per minute from 55° to 145°C Column inlet pressure using nitrogen as the carrier gas was 30 psig, corresponding to a flow of 50cc/min. Peak areas were measured with a planimeter and the composition of the product mixture was determined using the following equation

$$\% \, i = f_i A_i \, R/A_s$$

where f_i is the area factor (mg/unit area) for component i whose measured area is A_i, R the percent of the standard added to the sample and A_s the measured area of the internal standard

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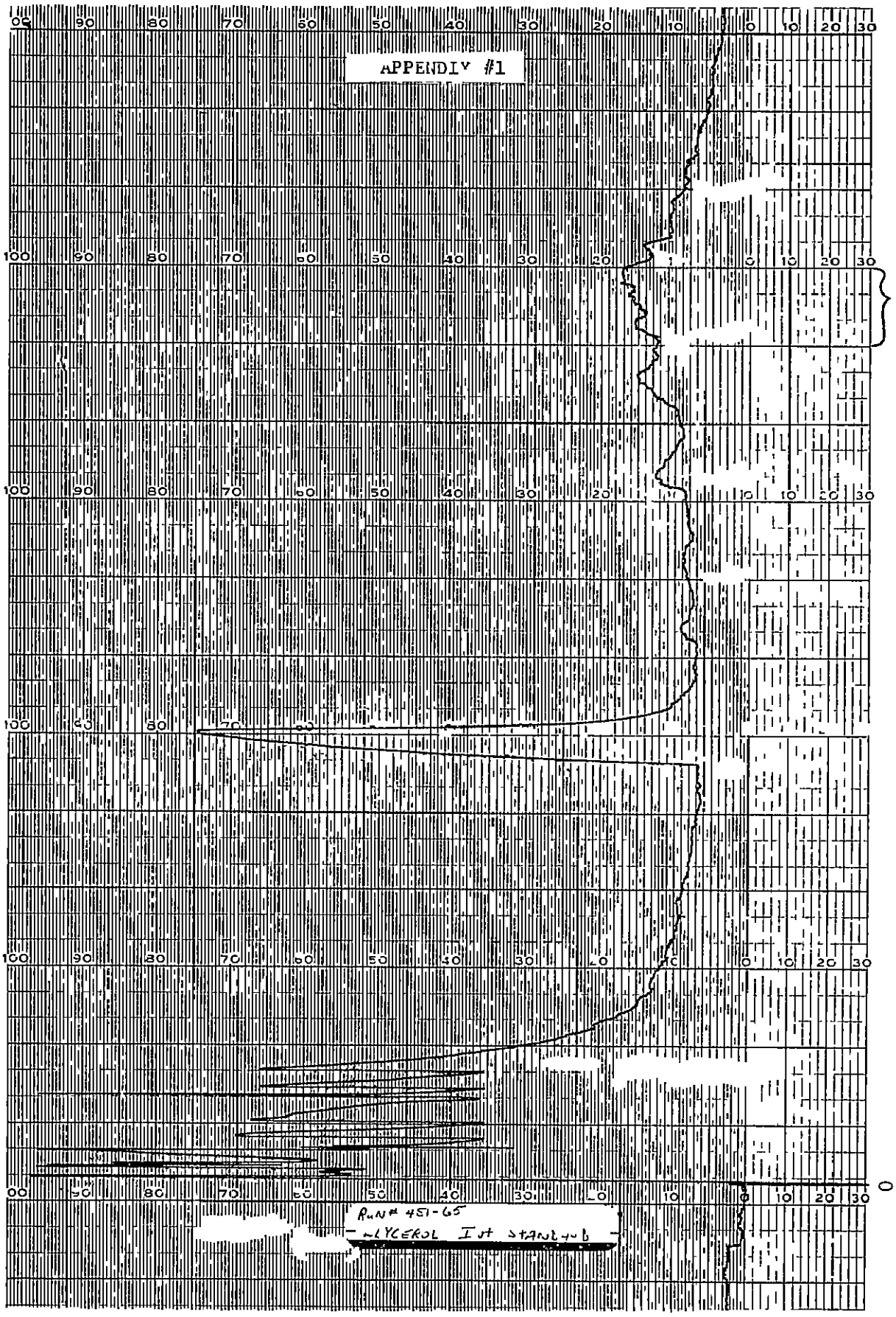
VII APPENDICES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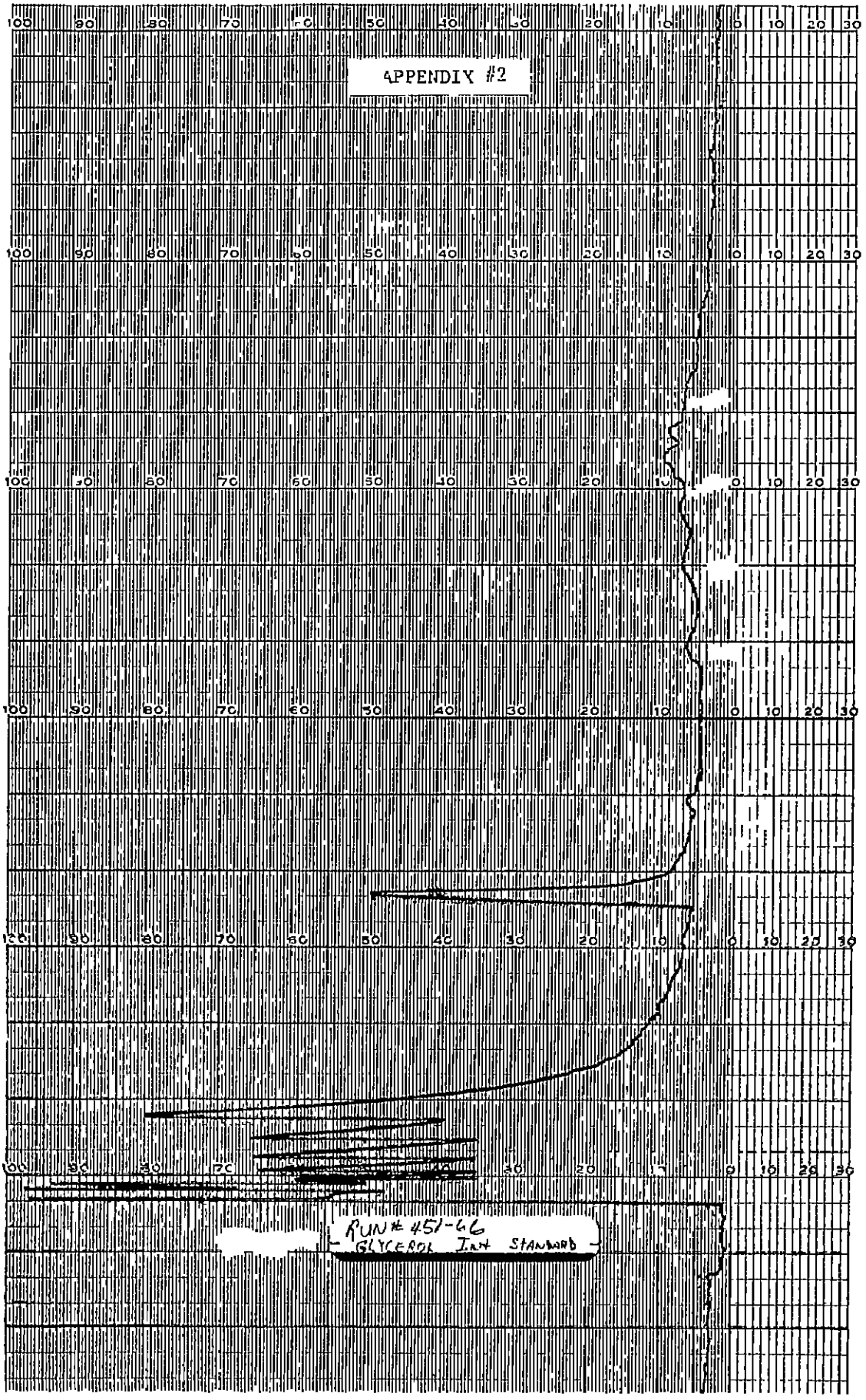
*each division corresponds to an elapsed time of one minute (equivalent to 10°C)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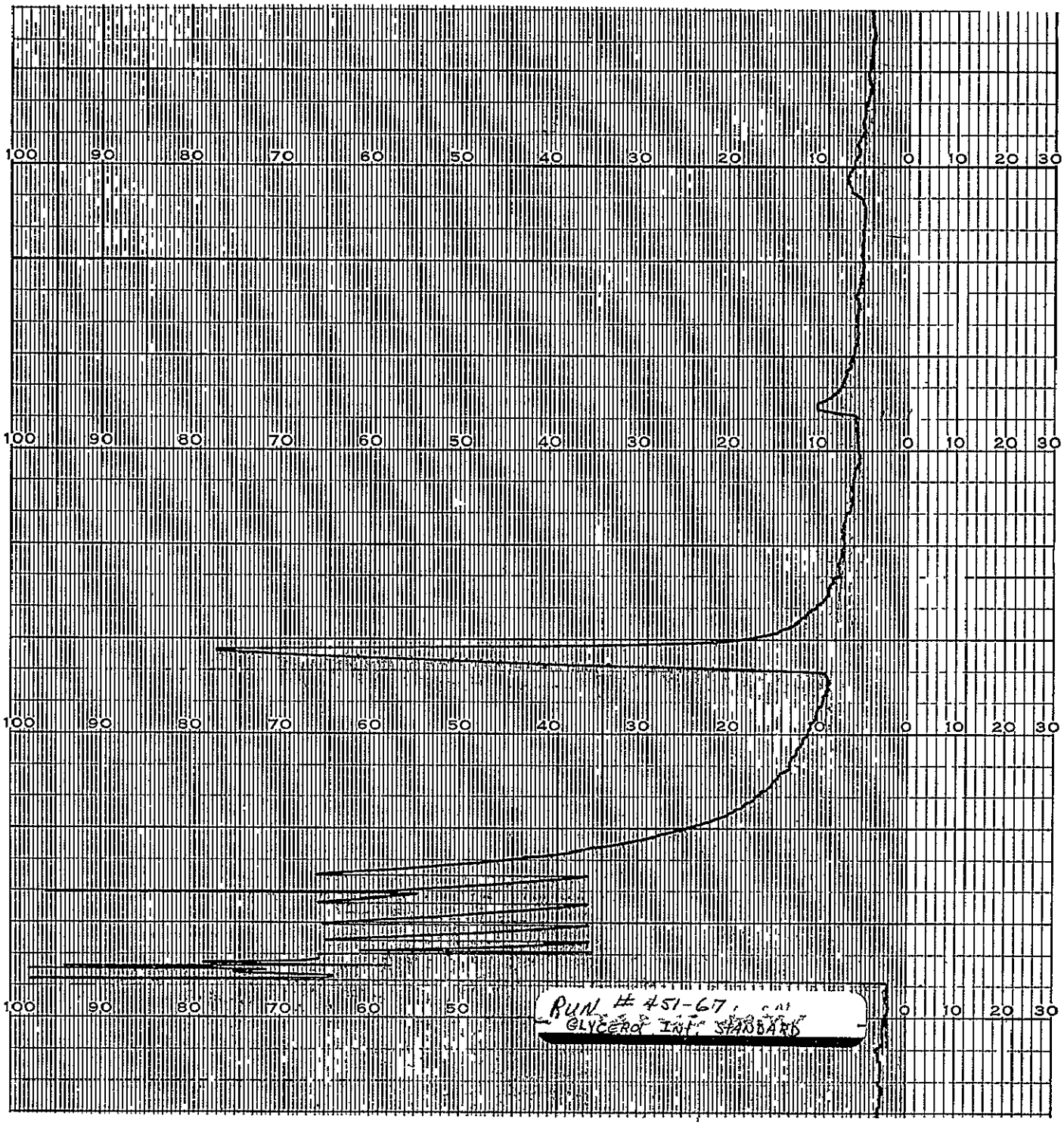
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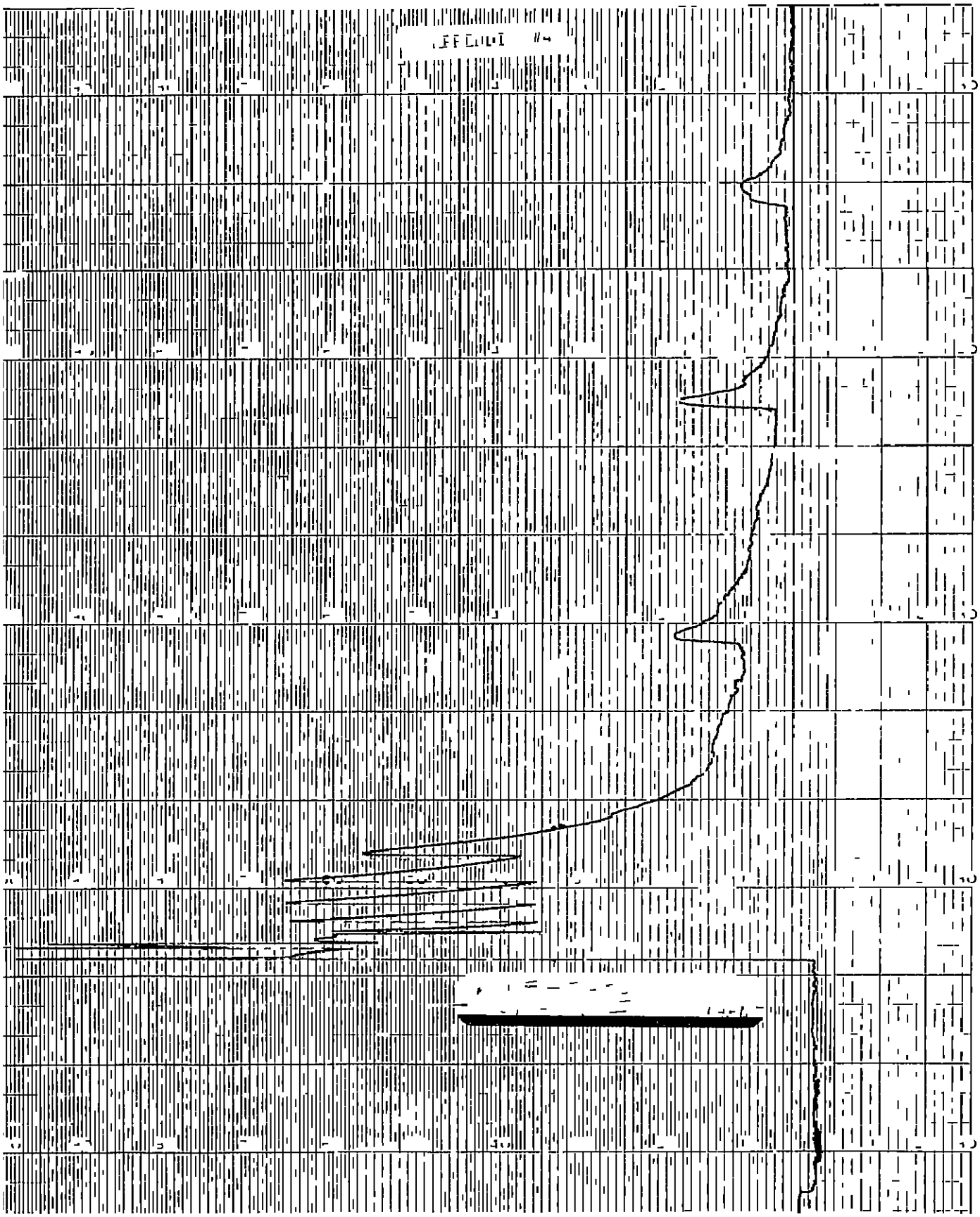

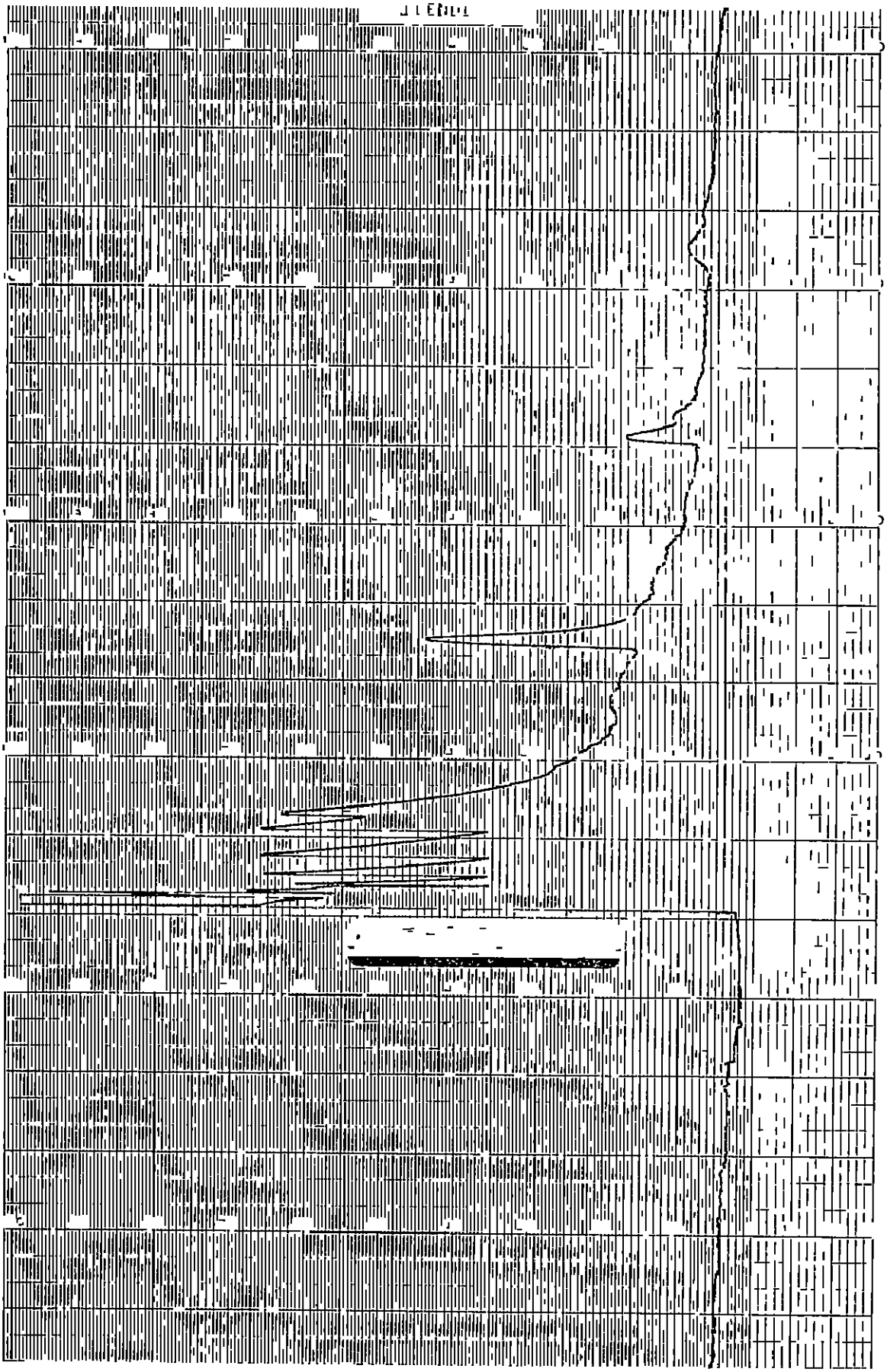

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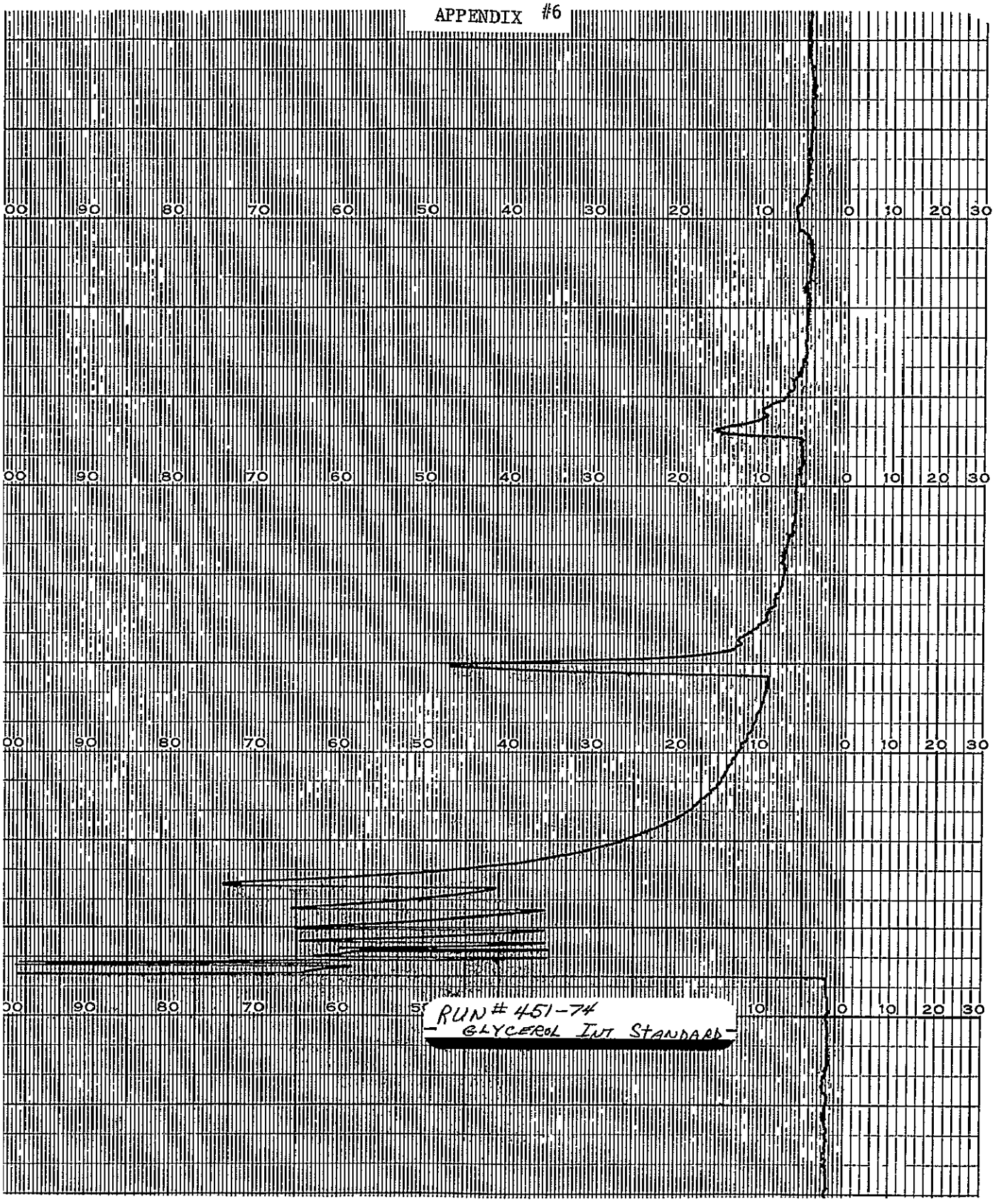

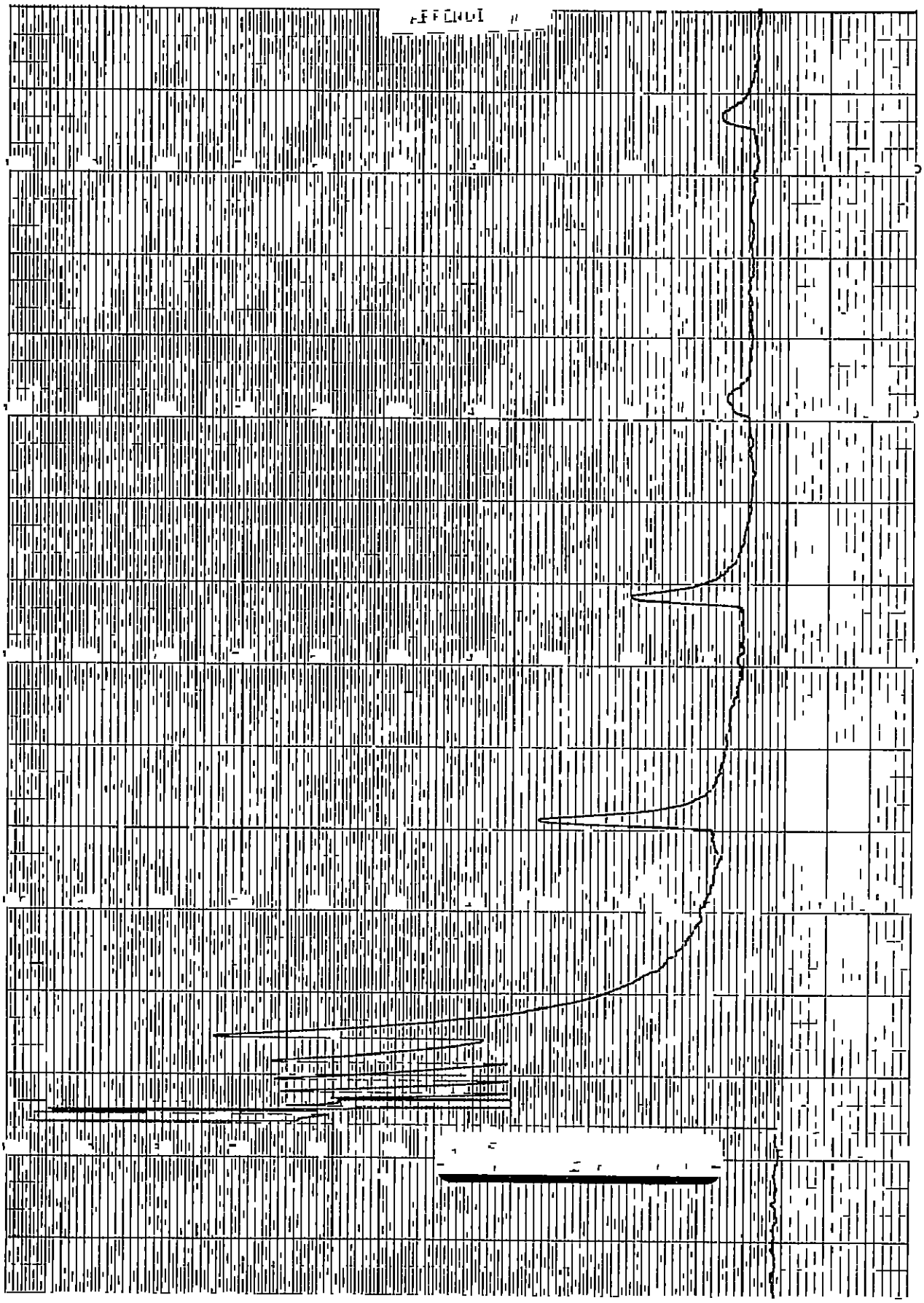

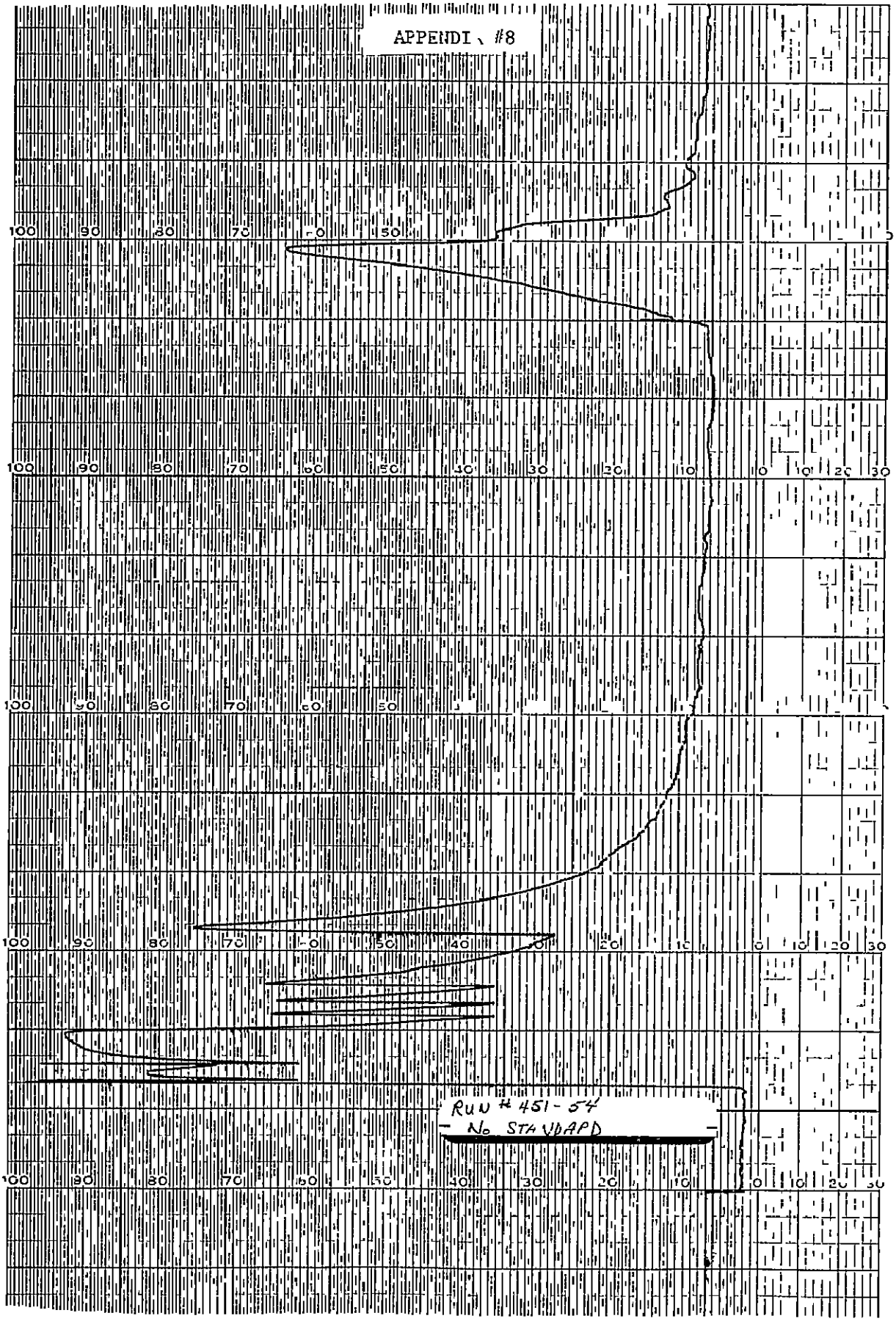
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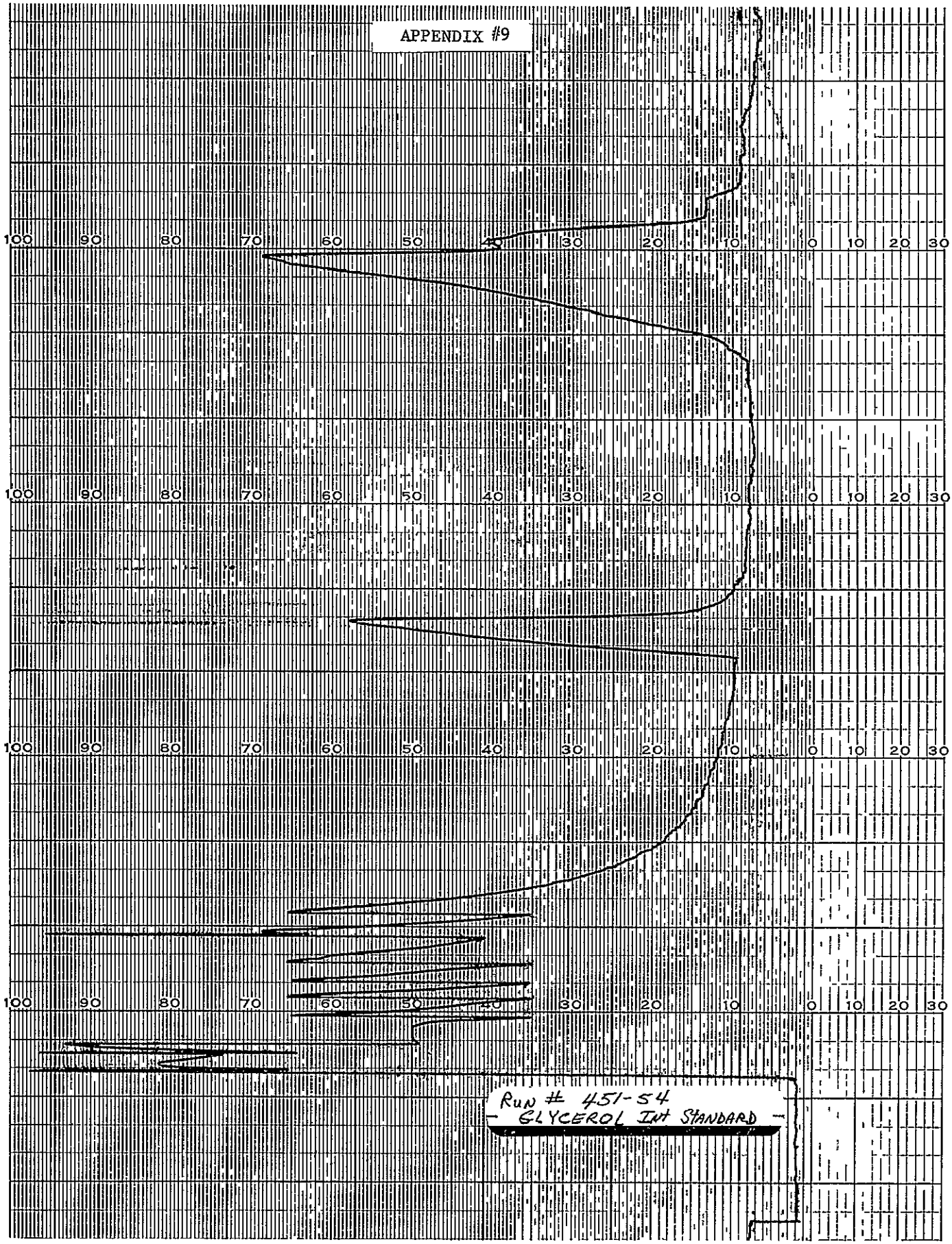
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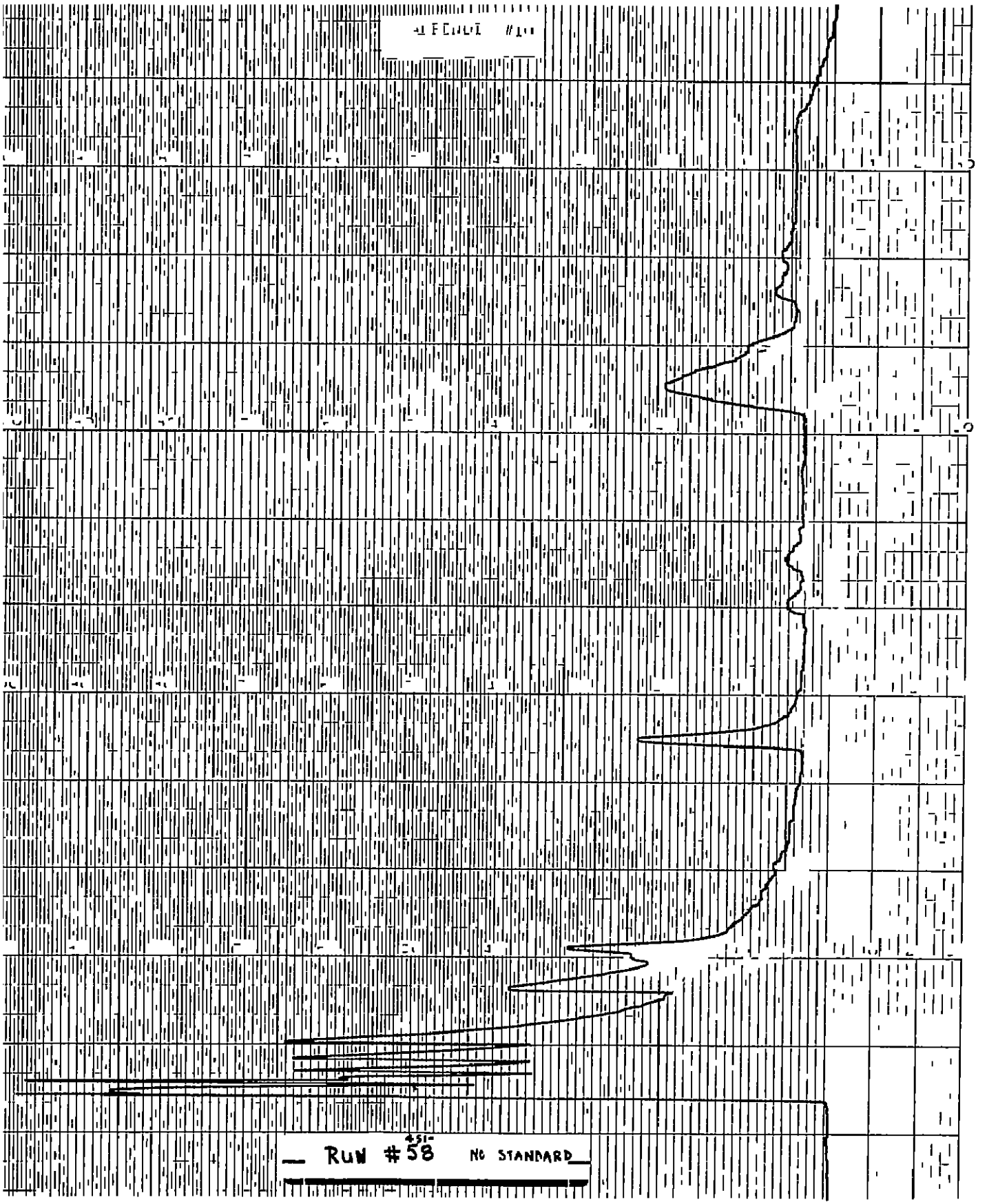
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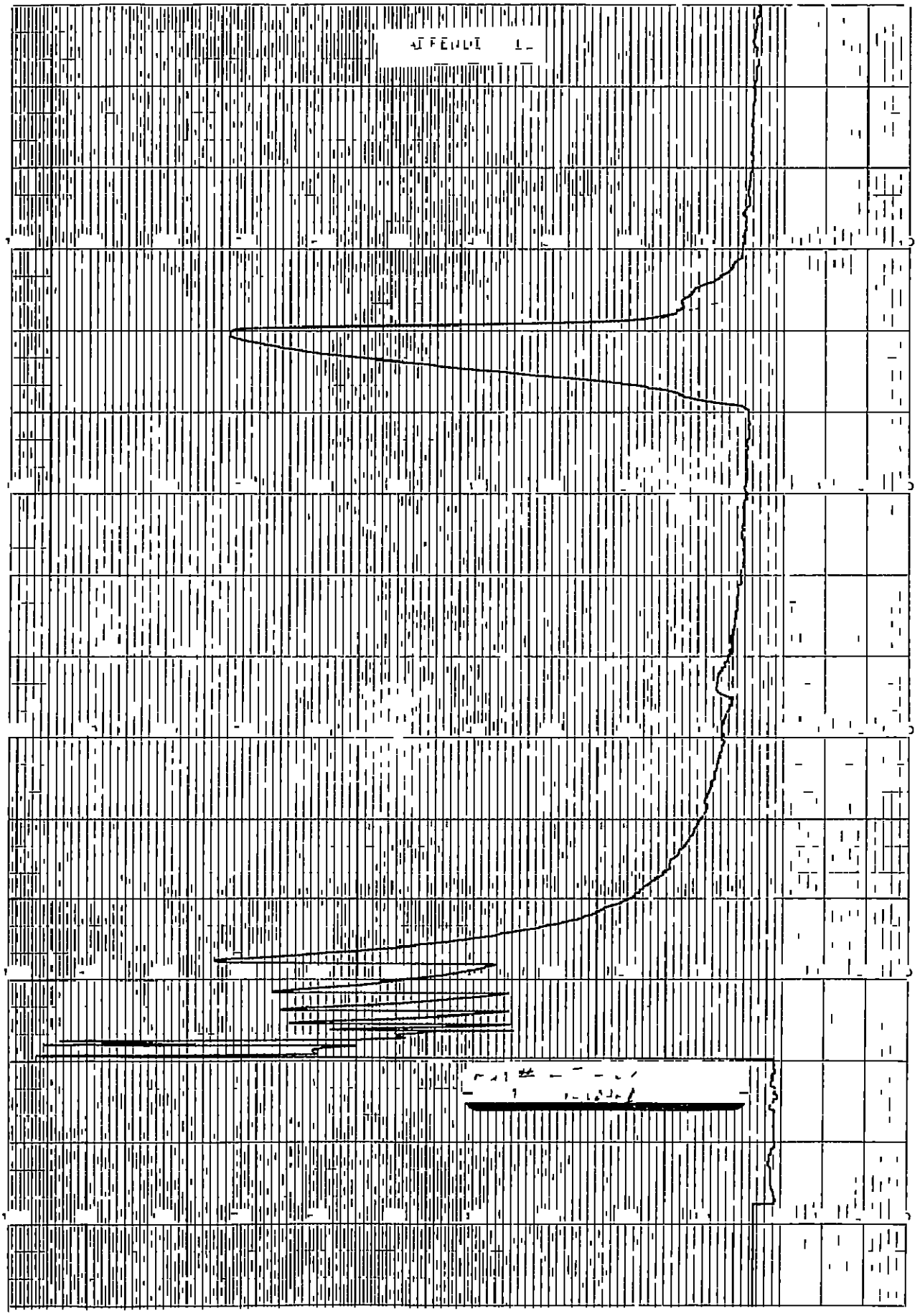

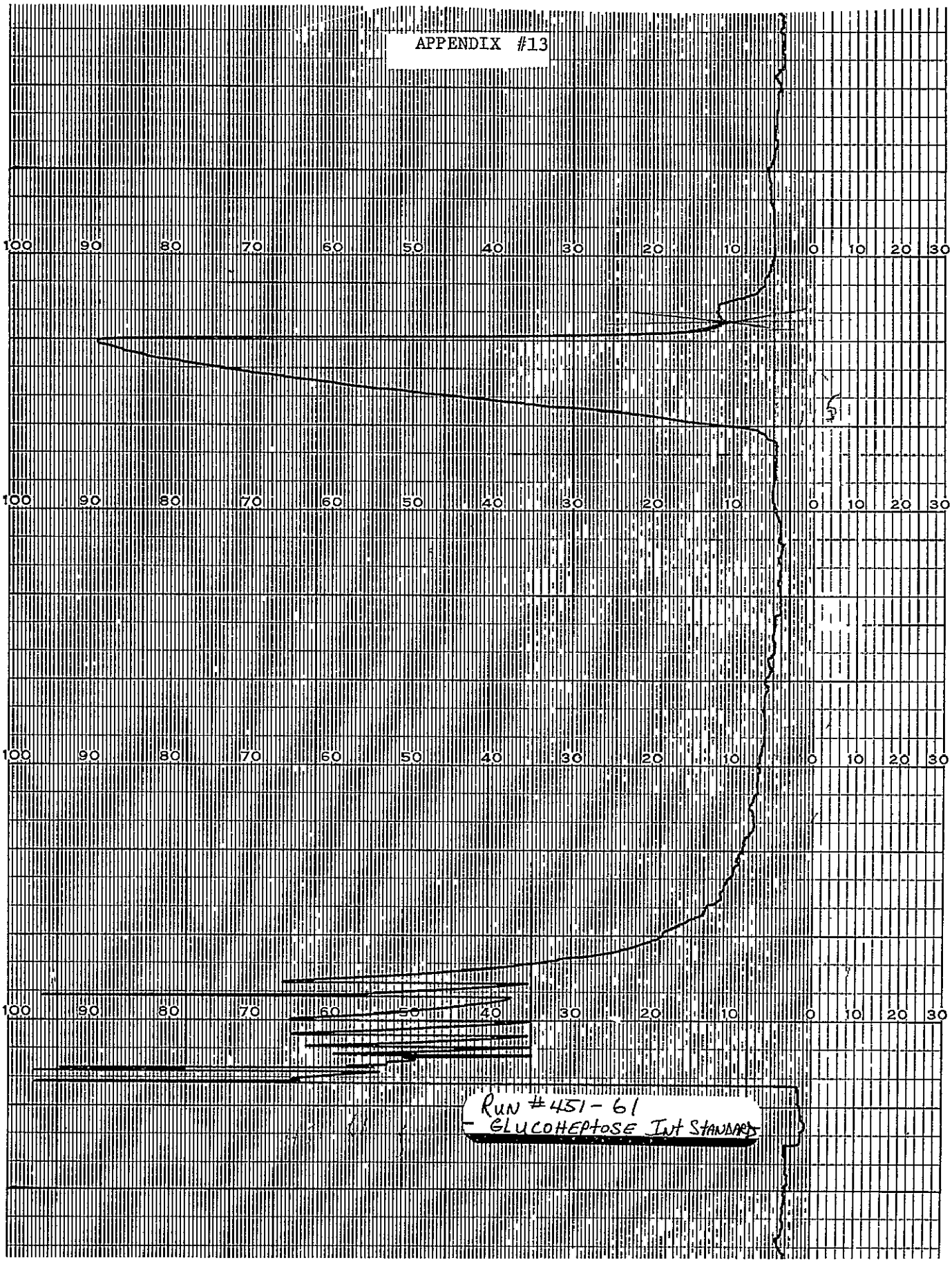
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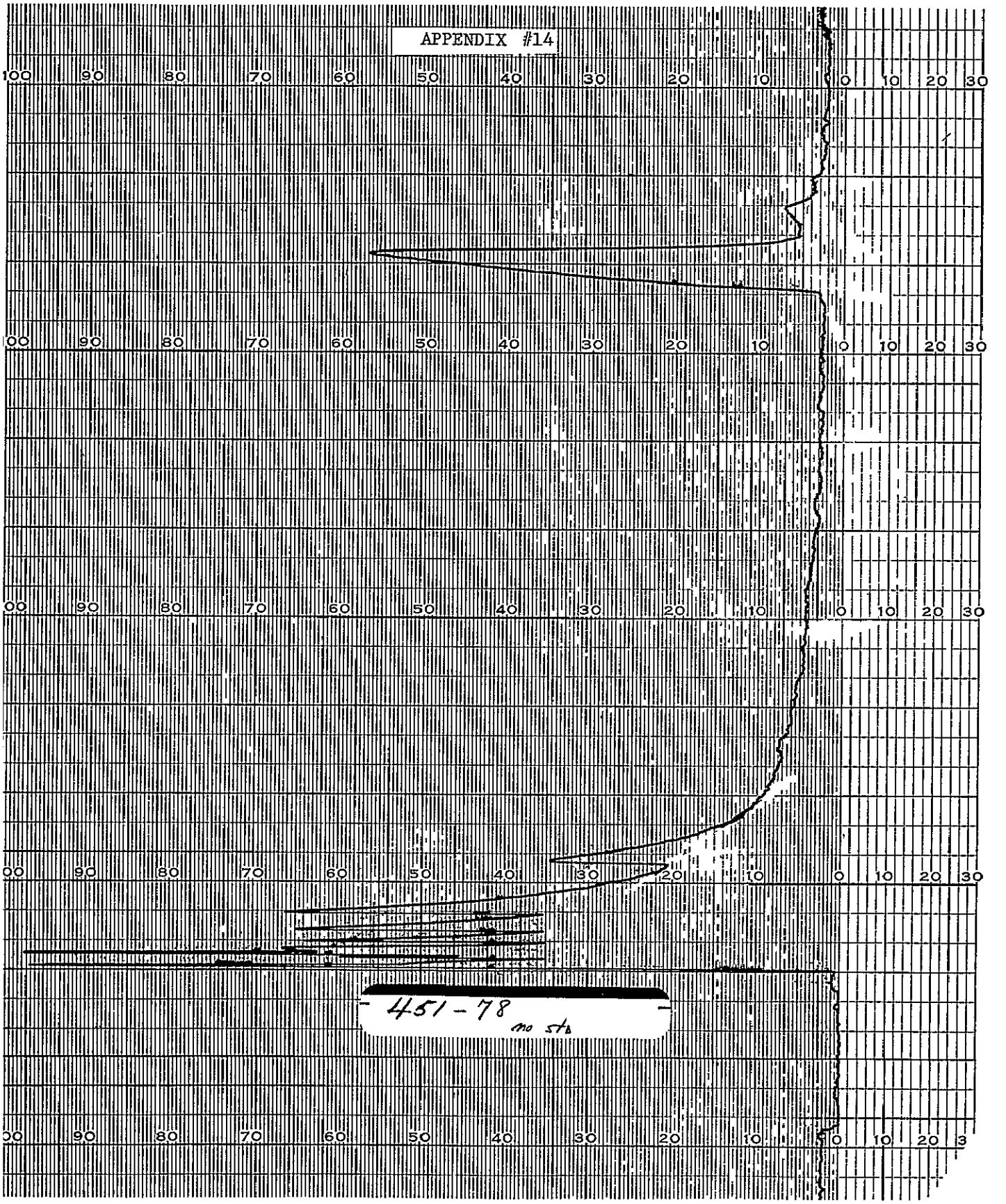
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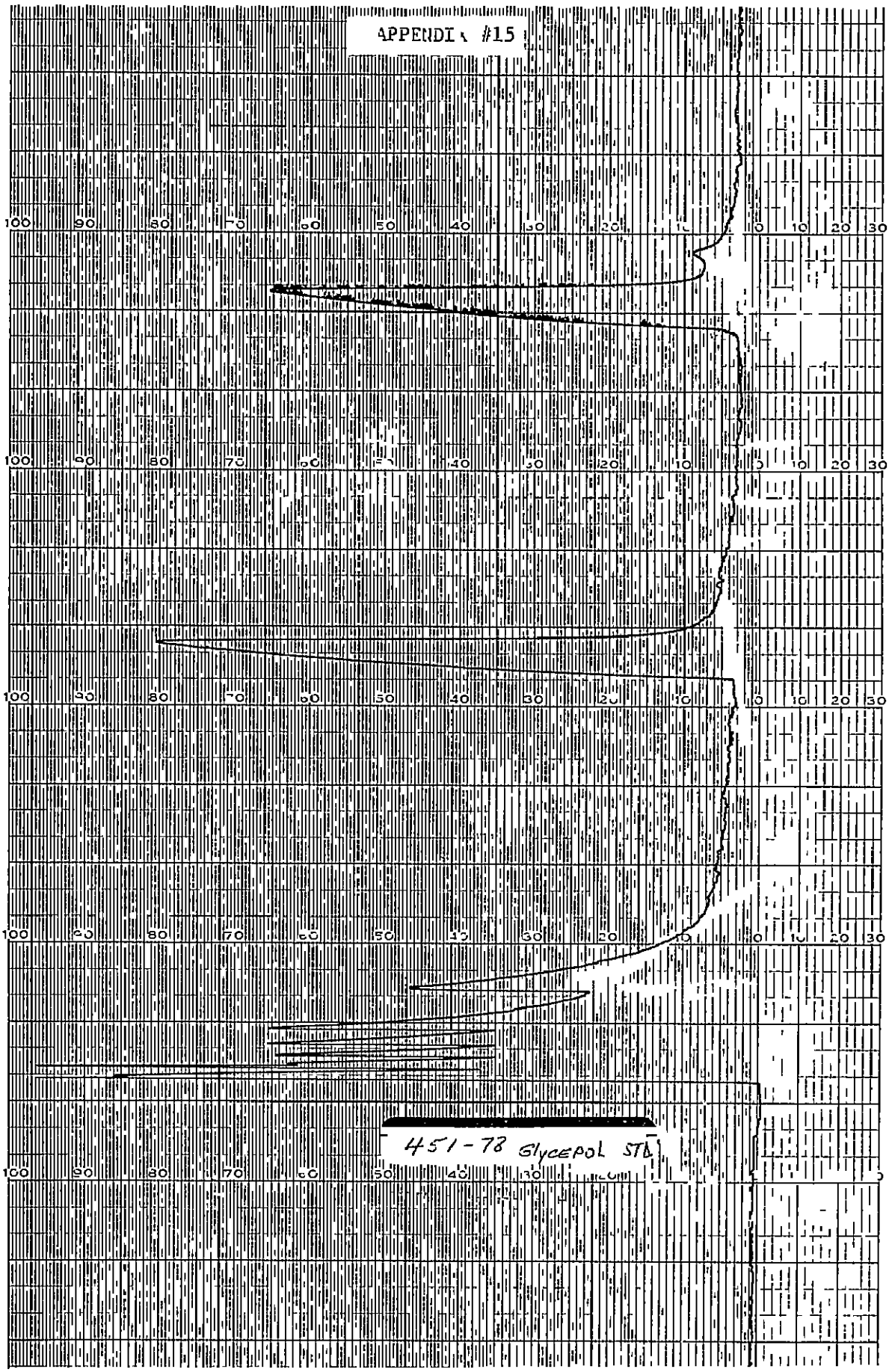
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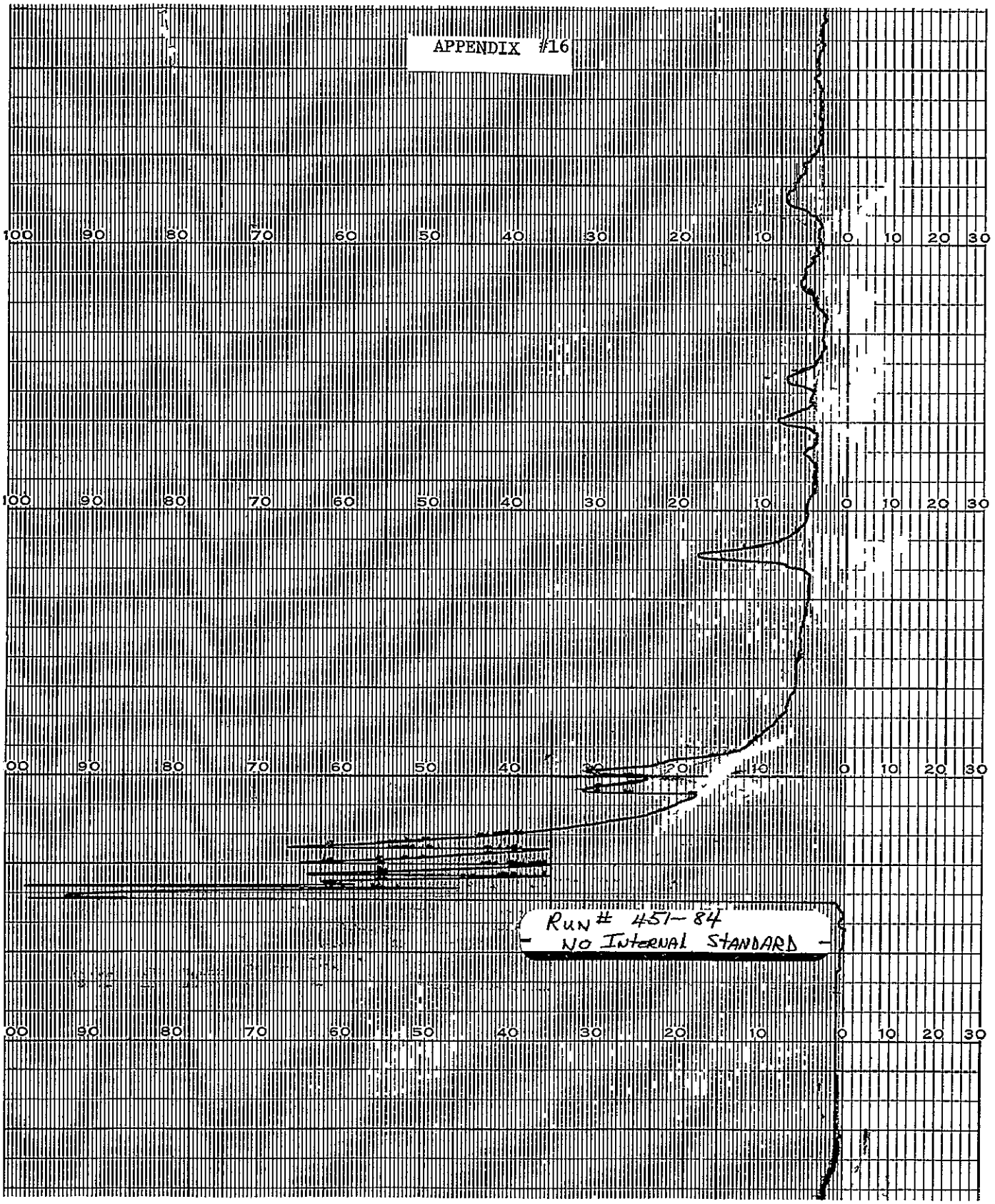
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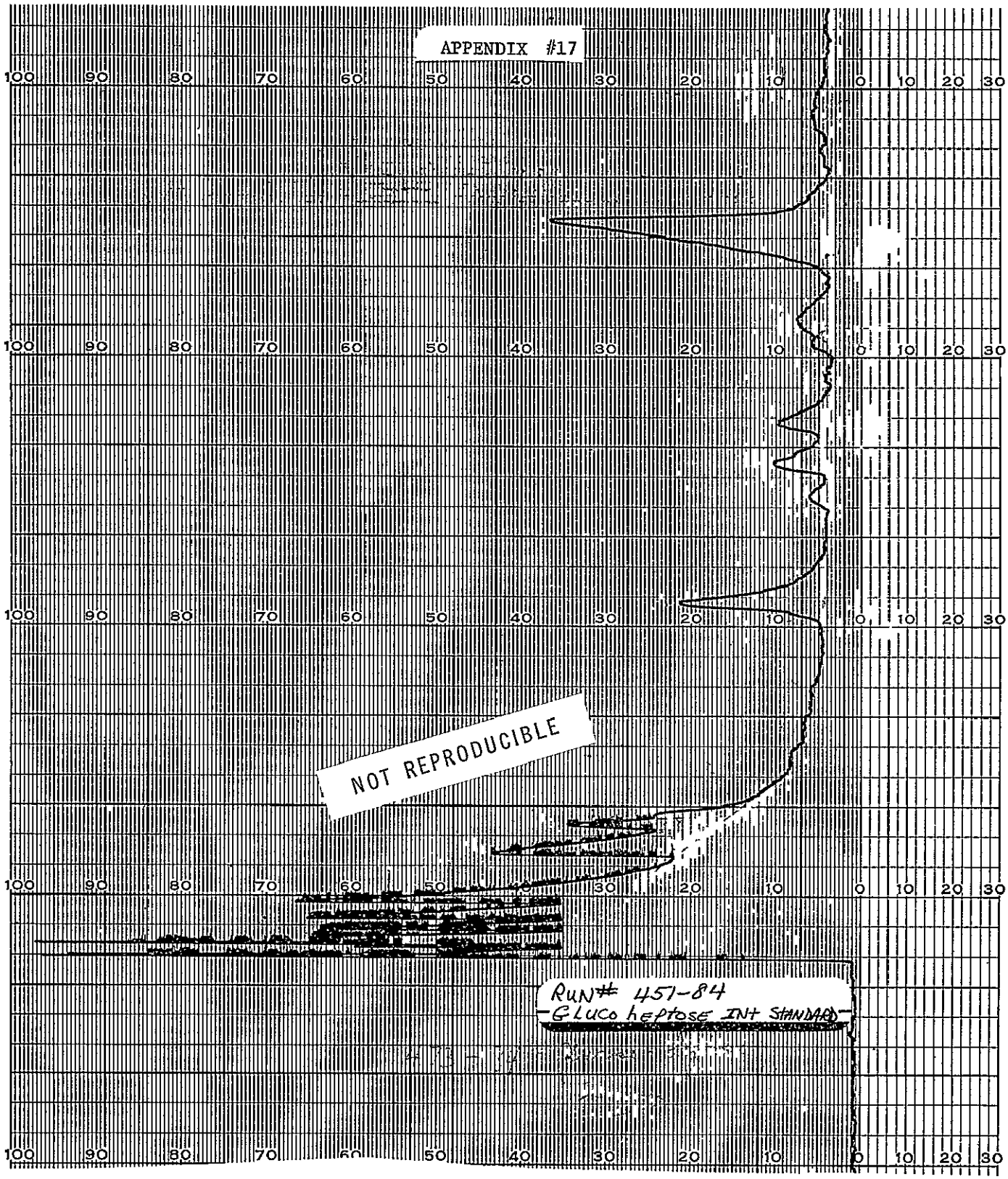
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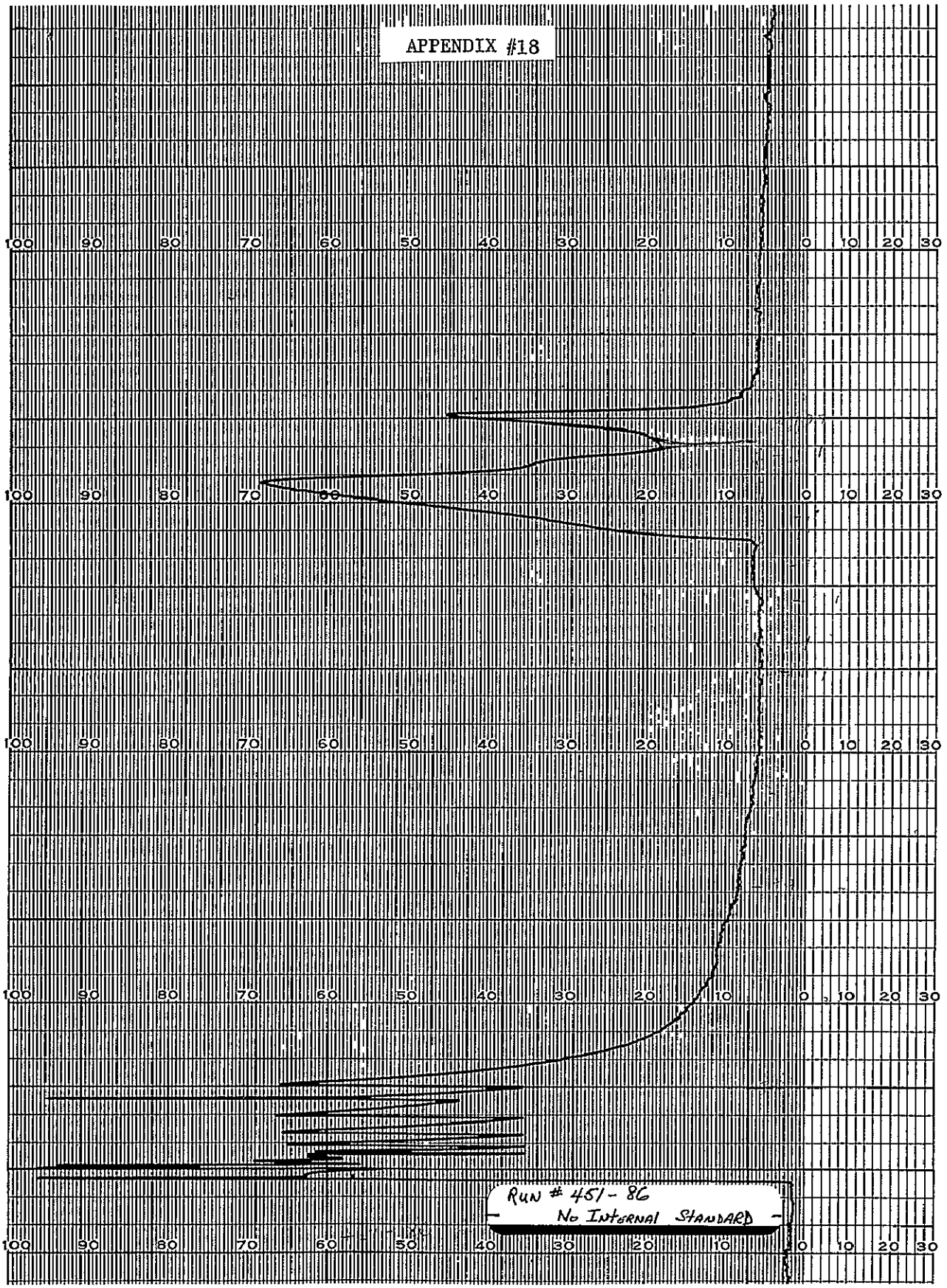
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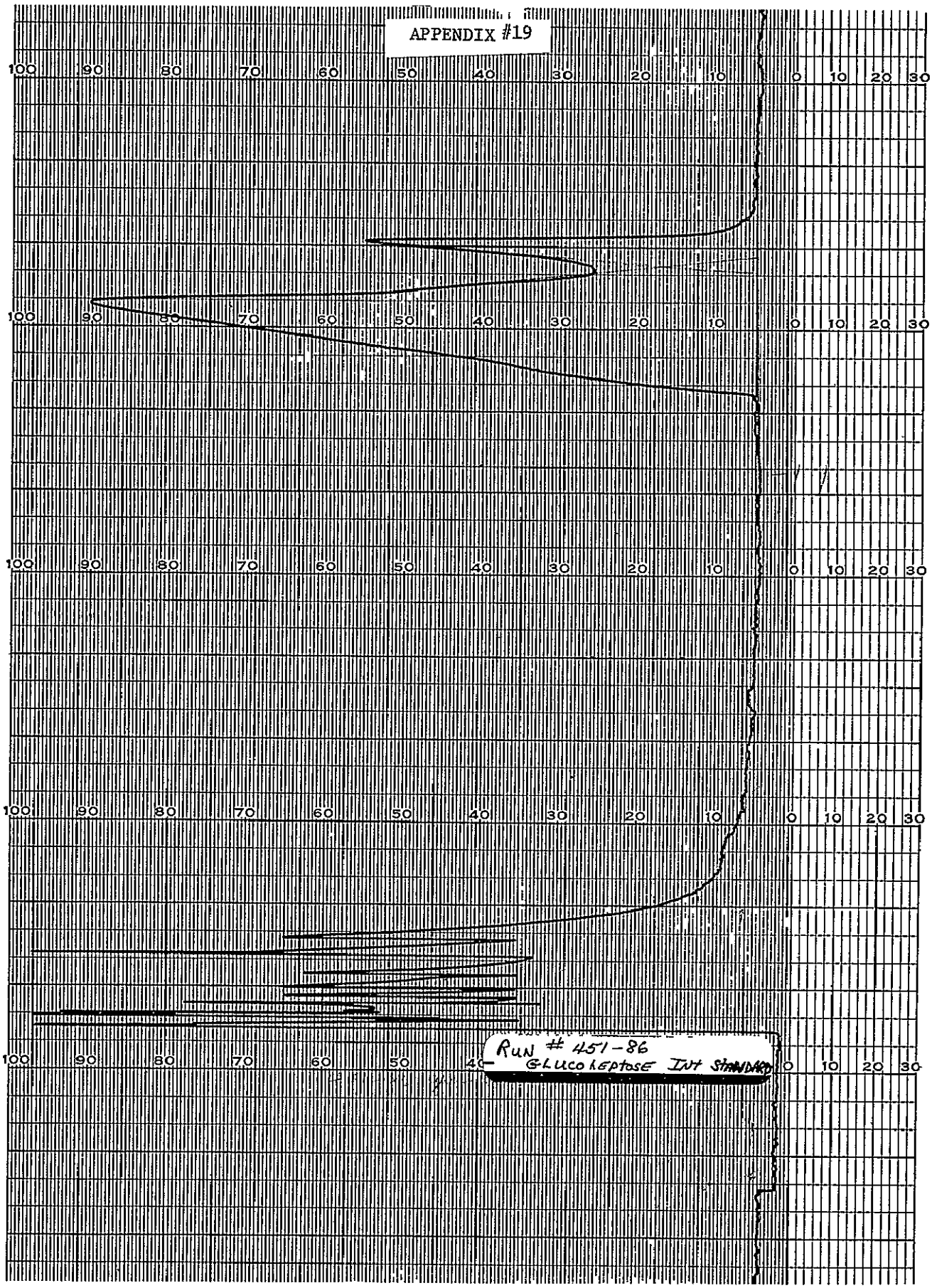
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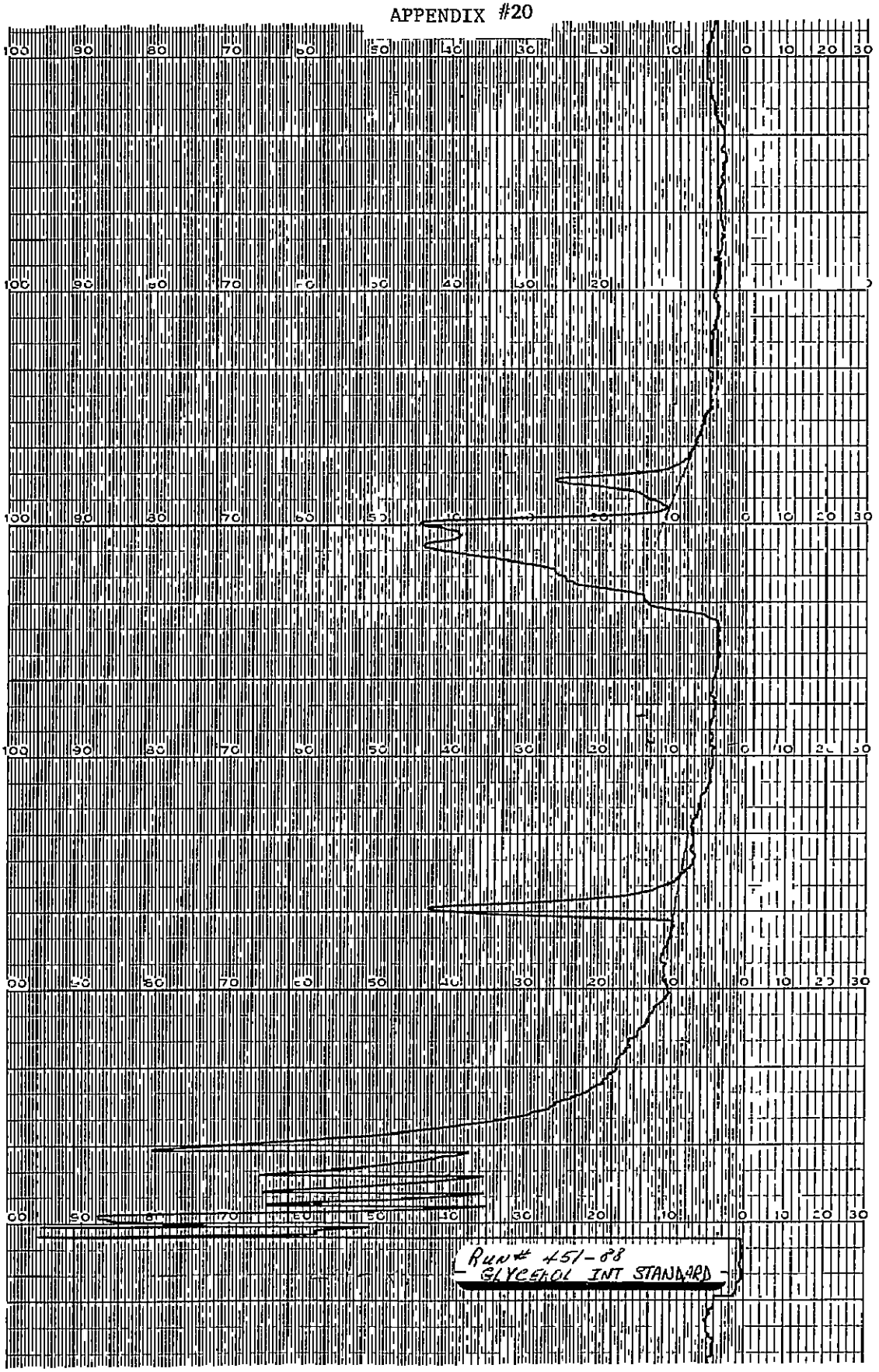

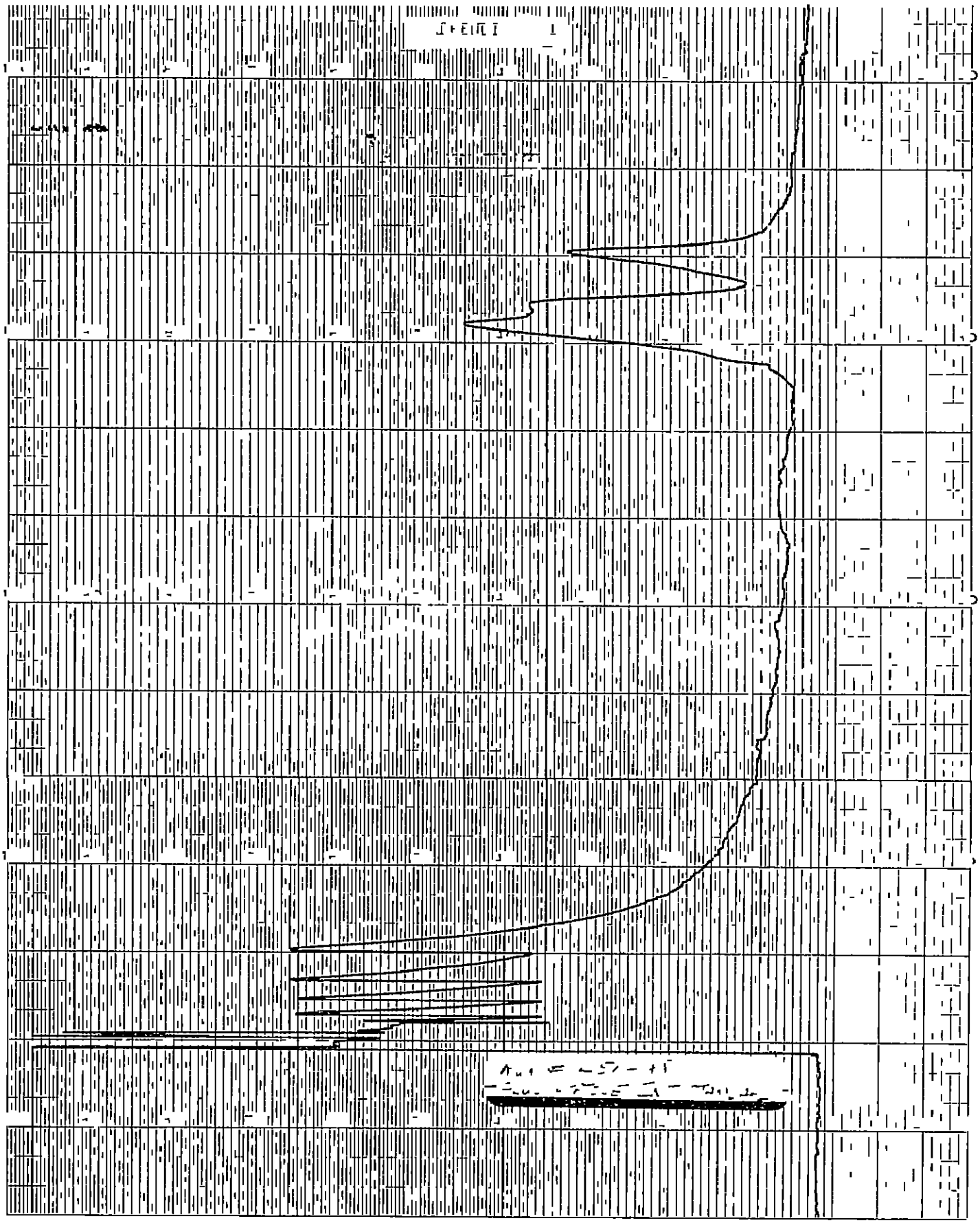

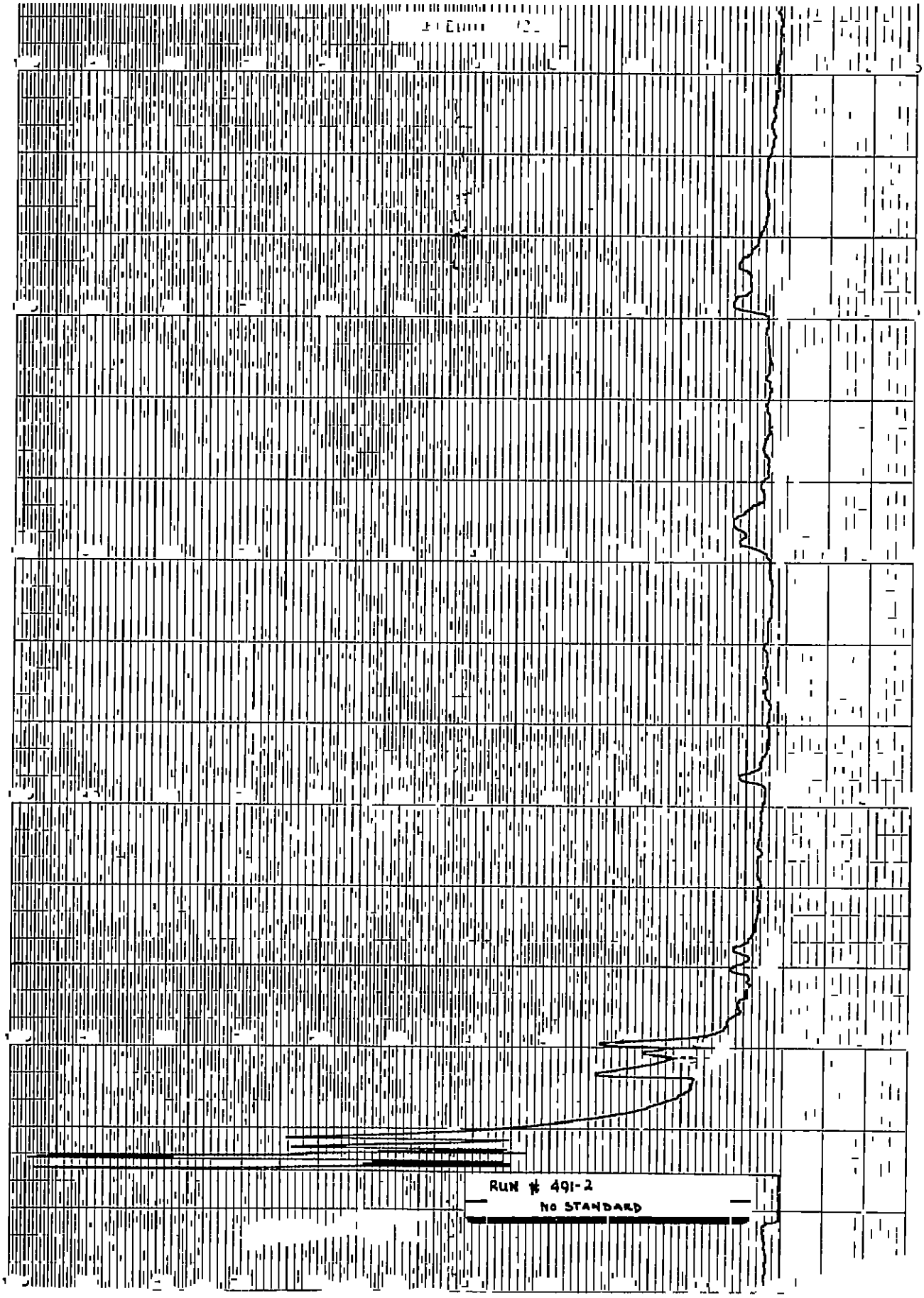
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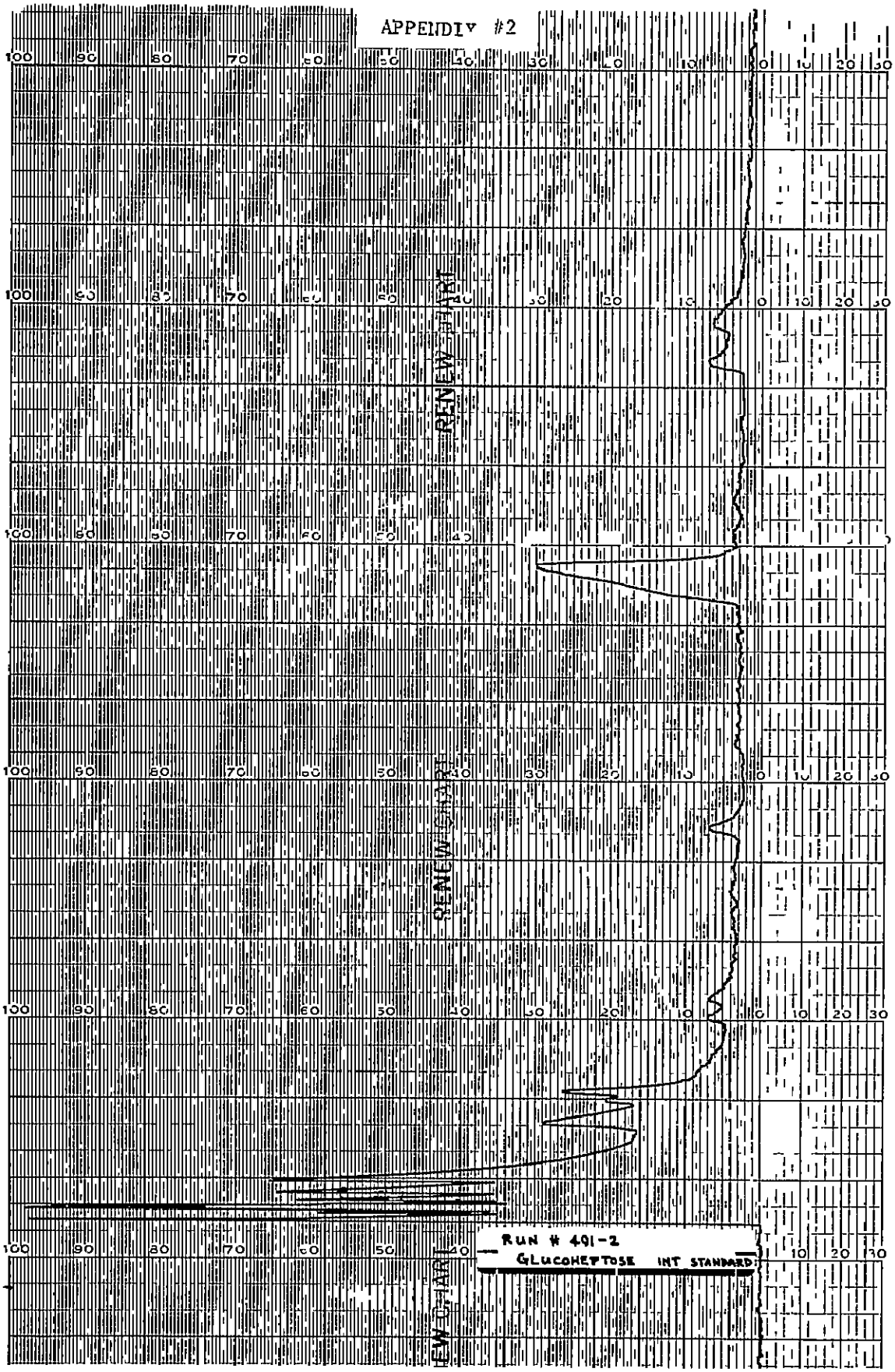
APPENDIX #2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RENEW CHART
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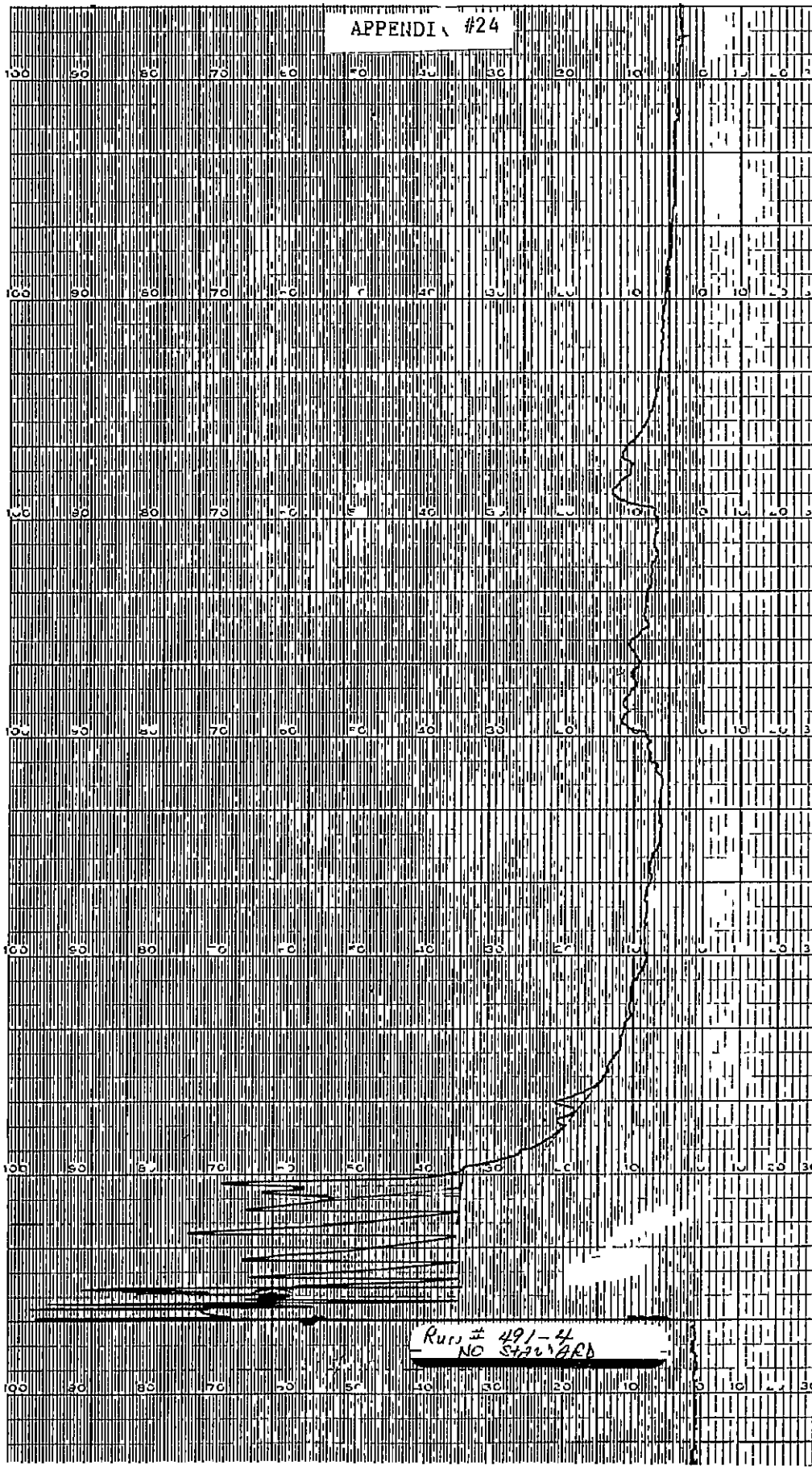
GLUCOHEPTOSE INT STANDARD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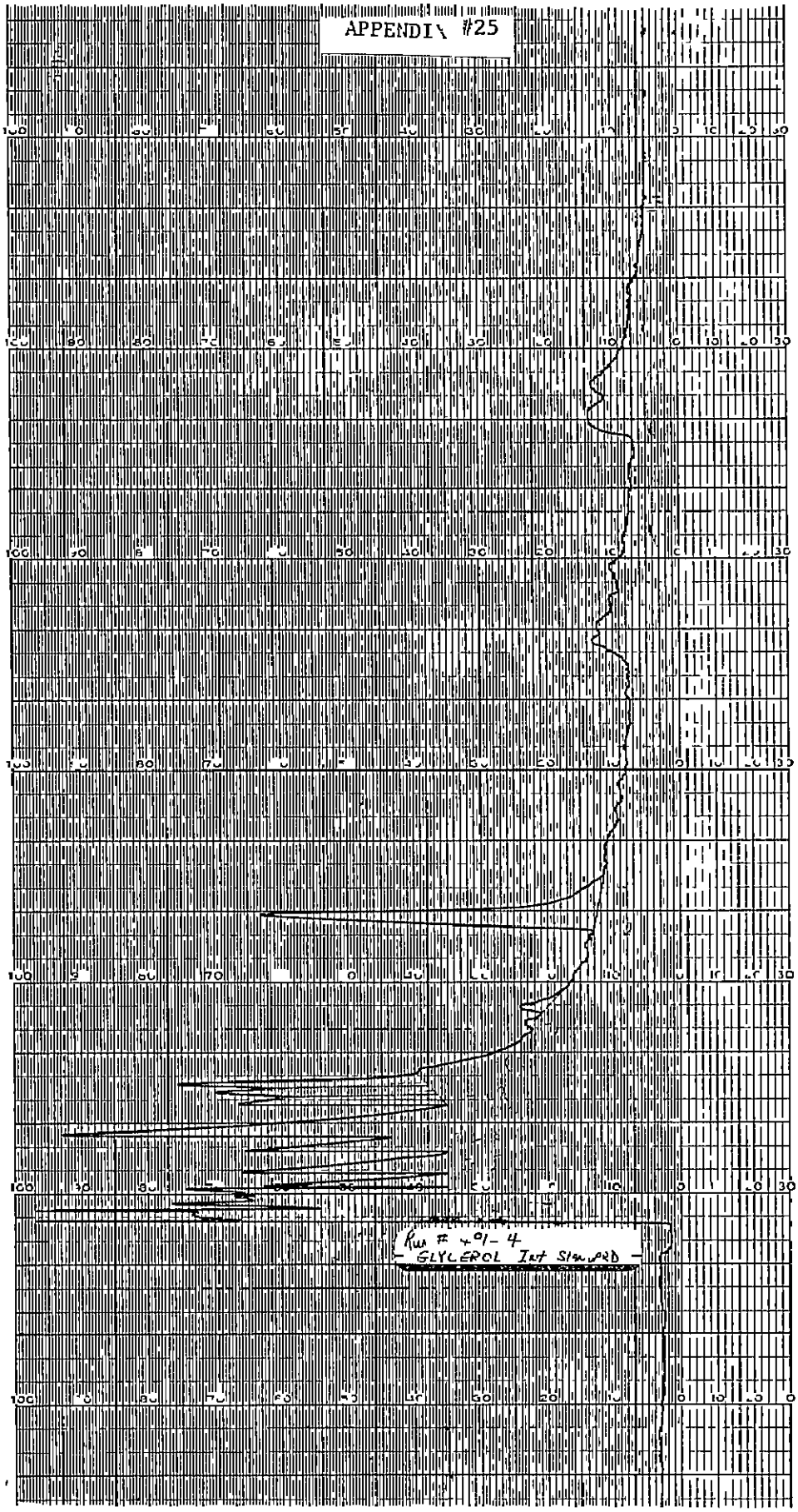
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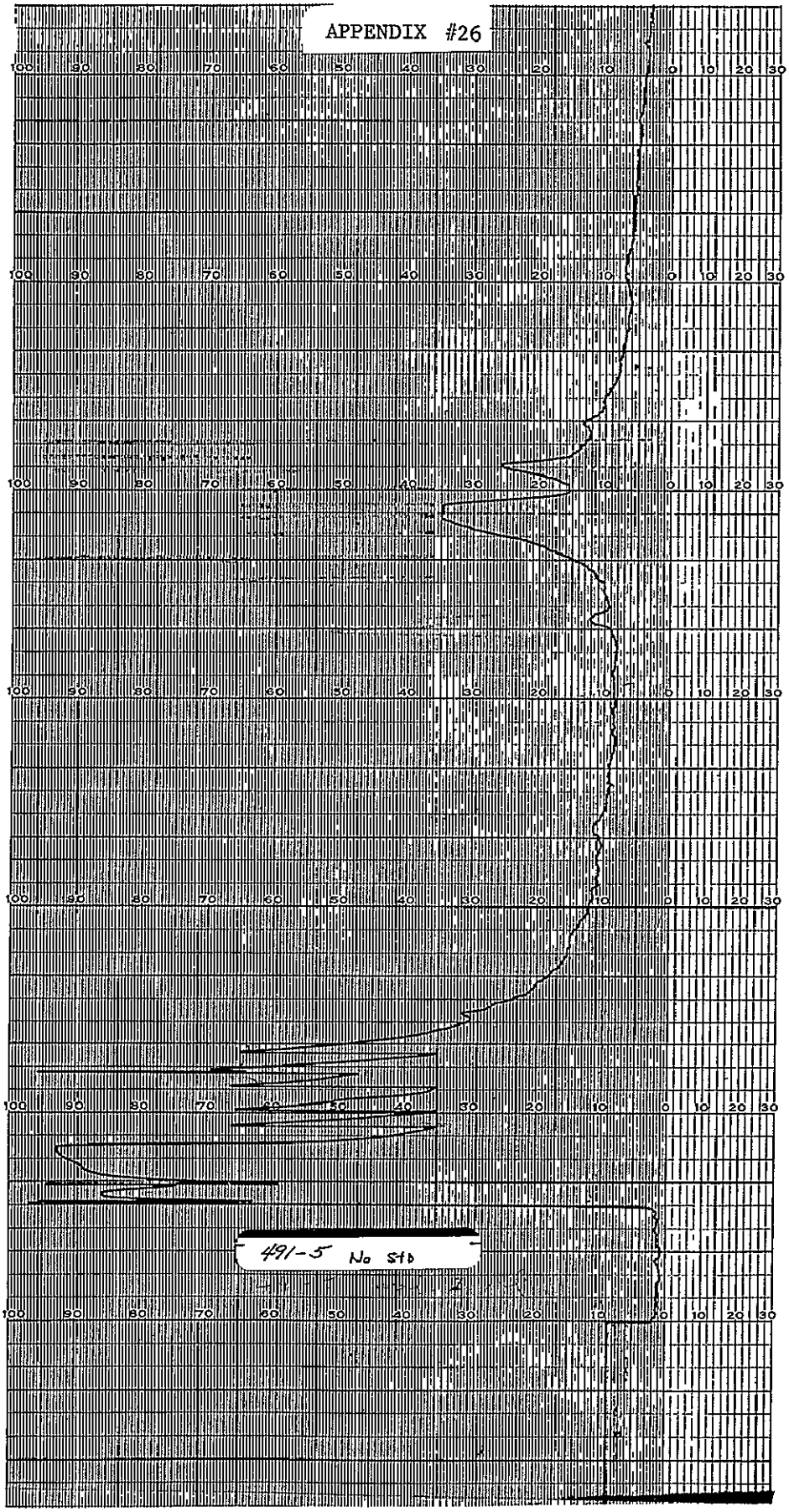
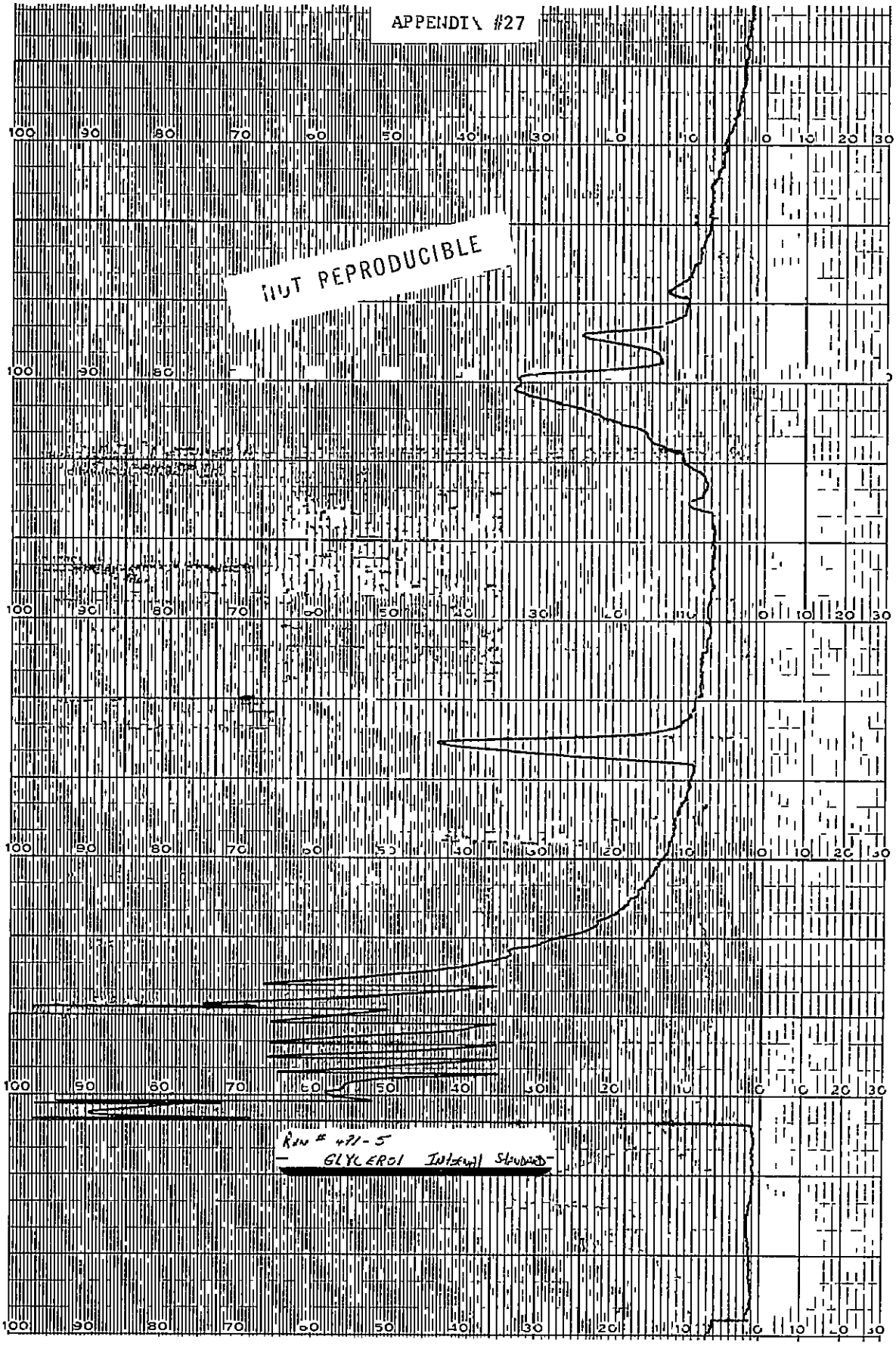
APPENDIX #26

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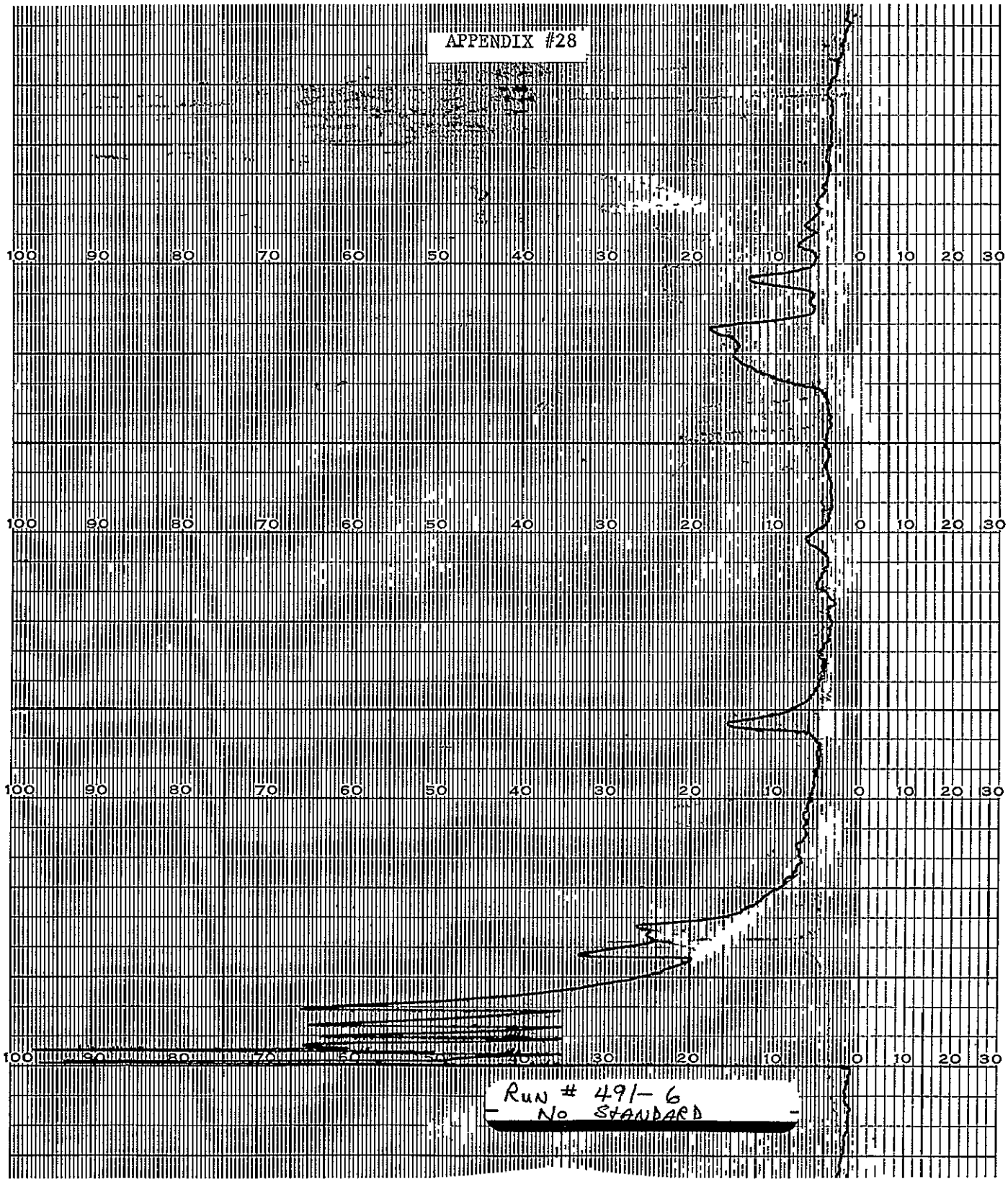
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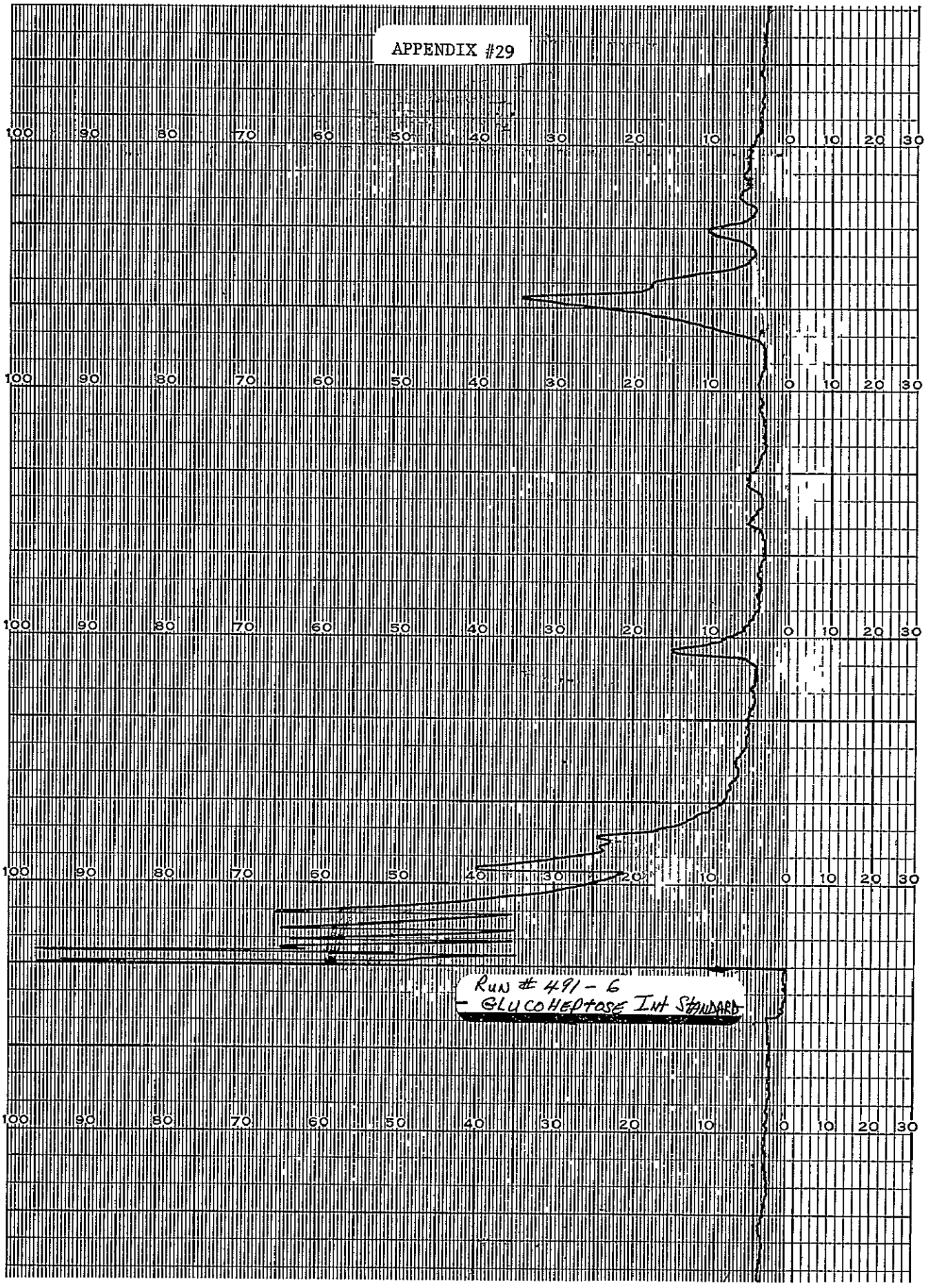
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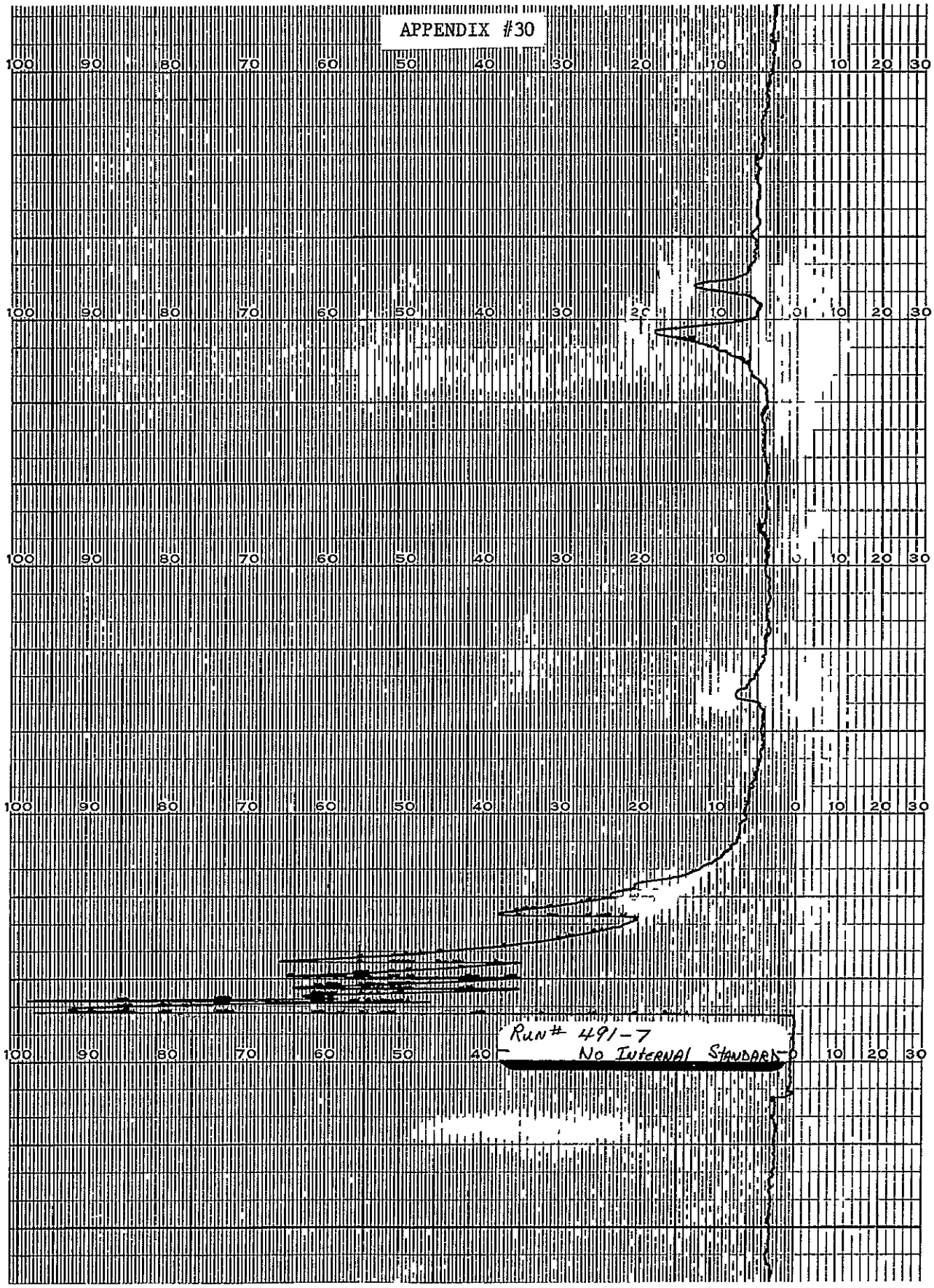
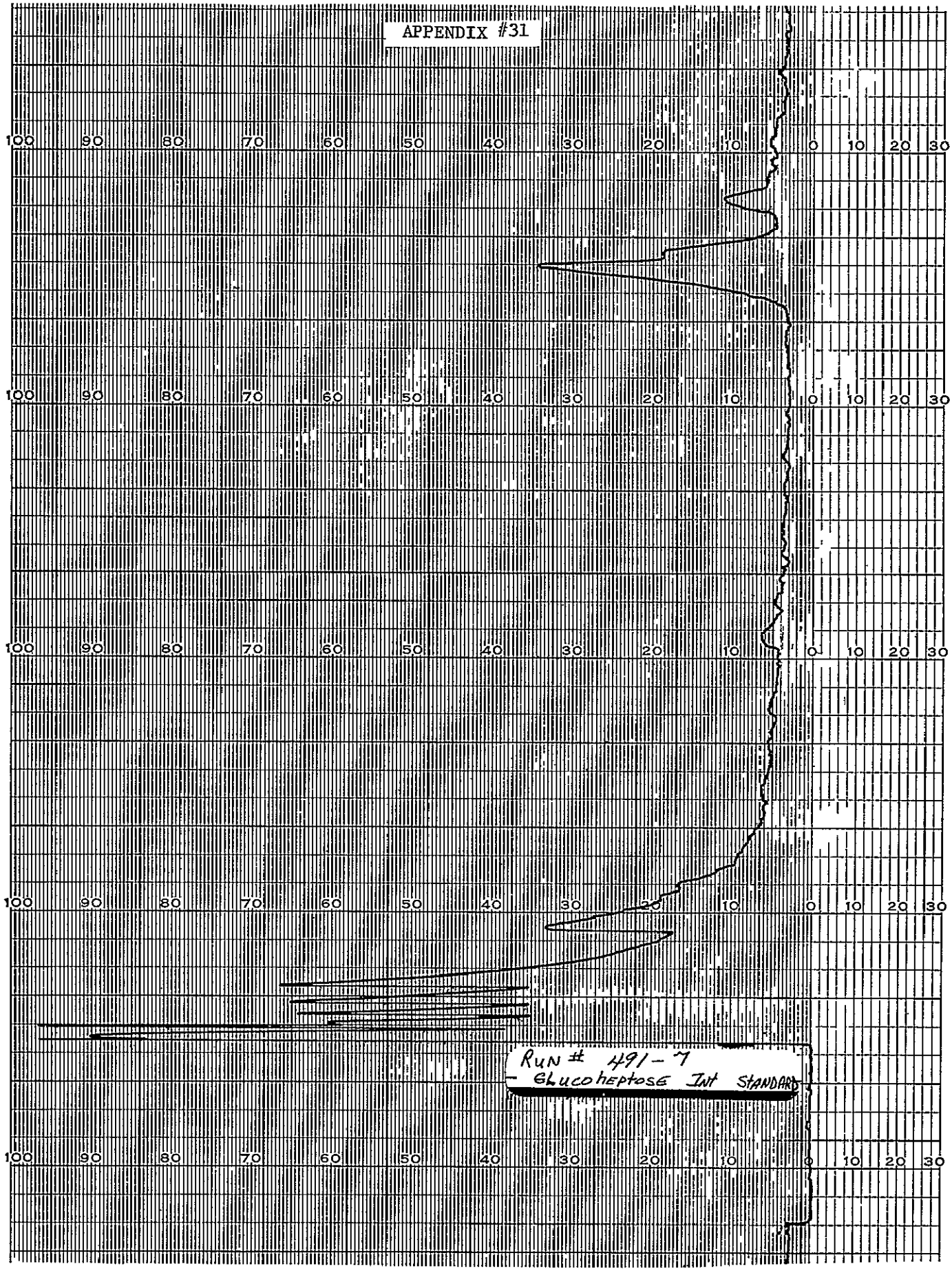
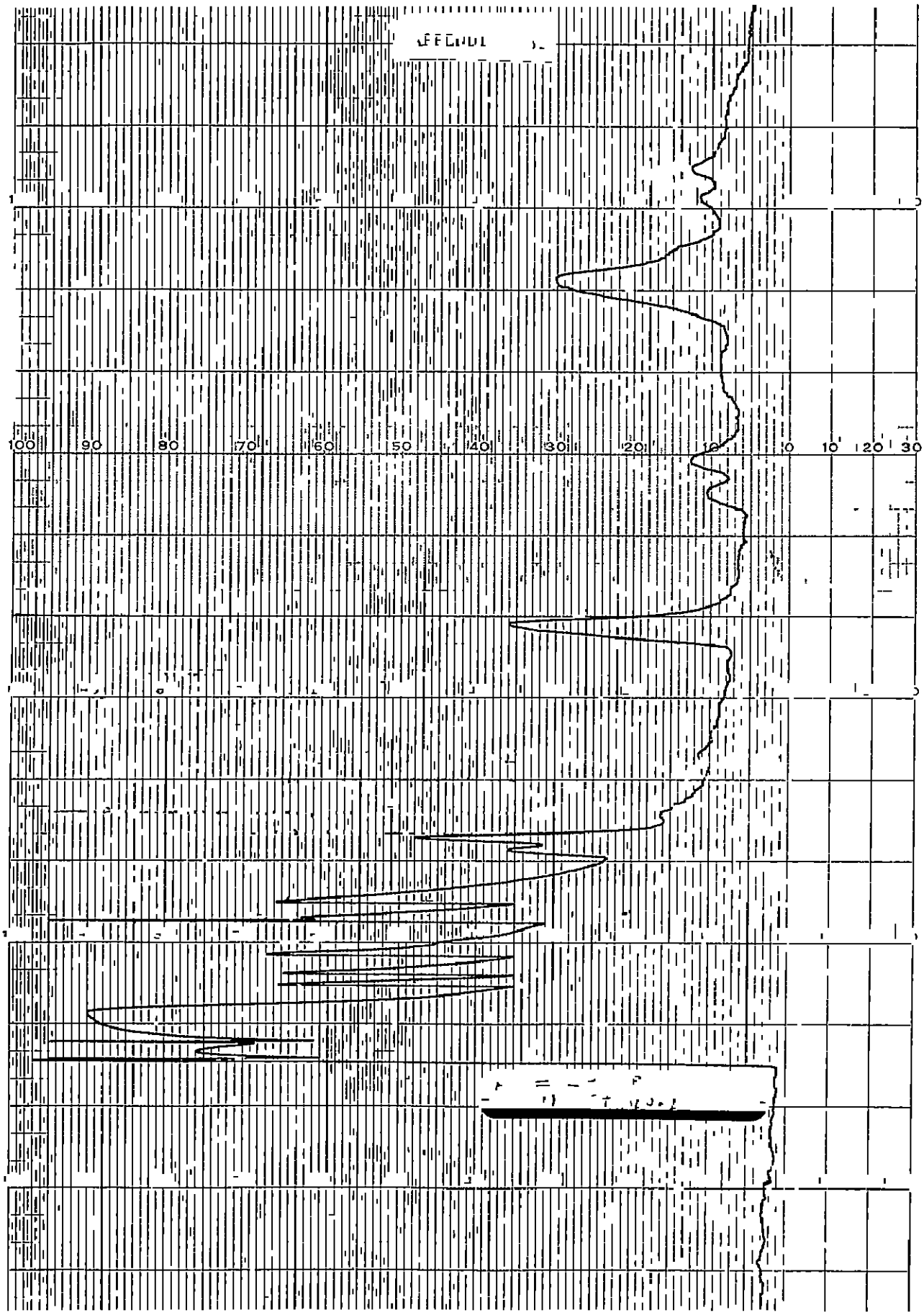
- GLUCOHEPTOSE INT STANDARD

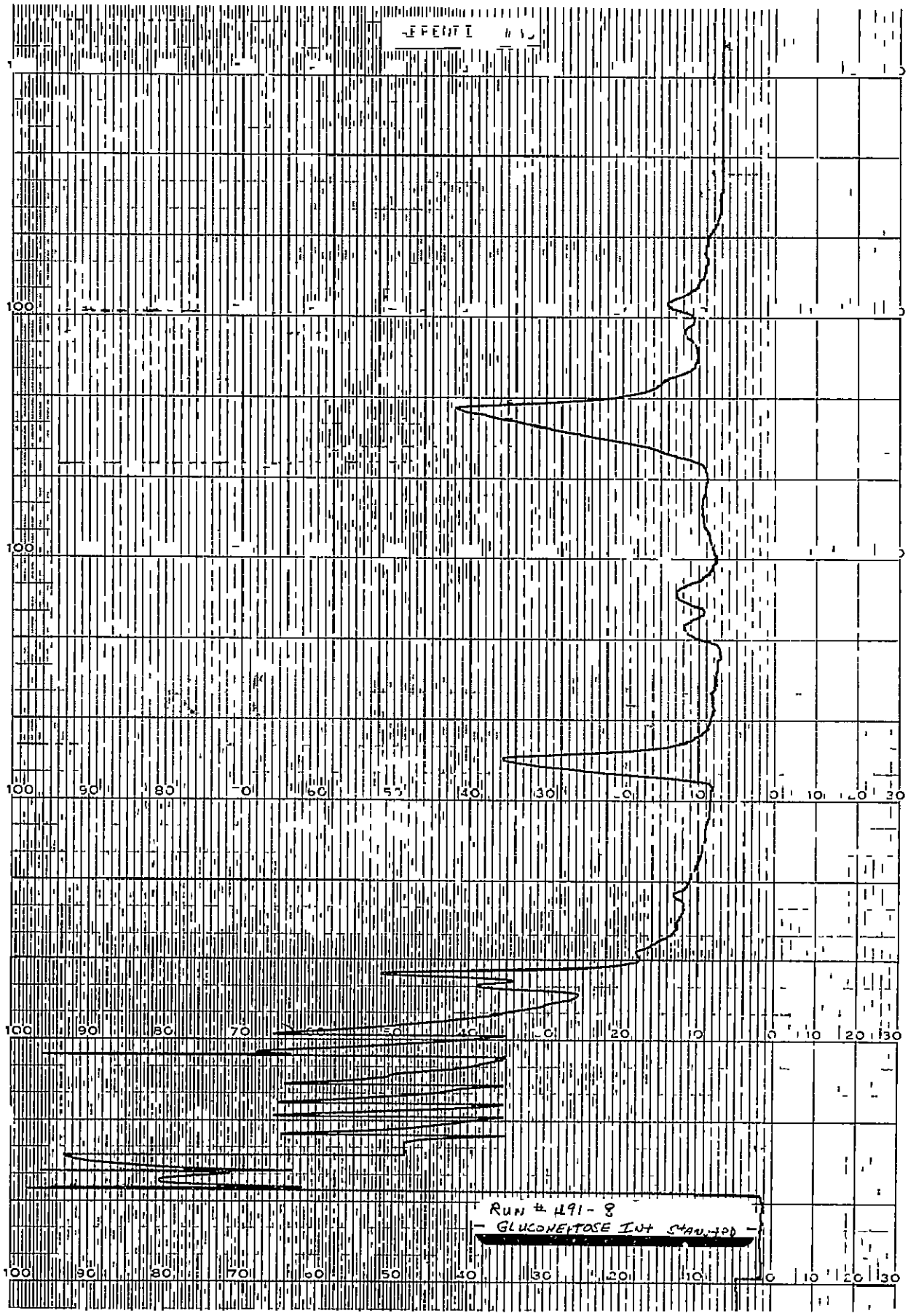
APPENDIX #30

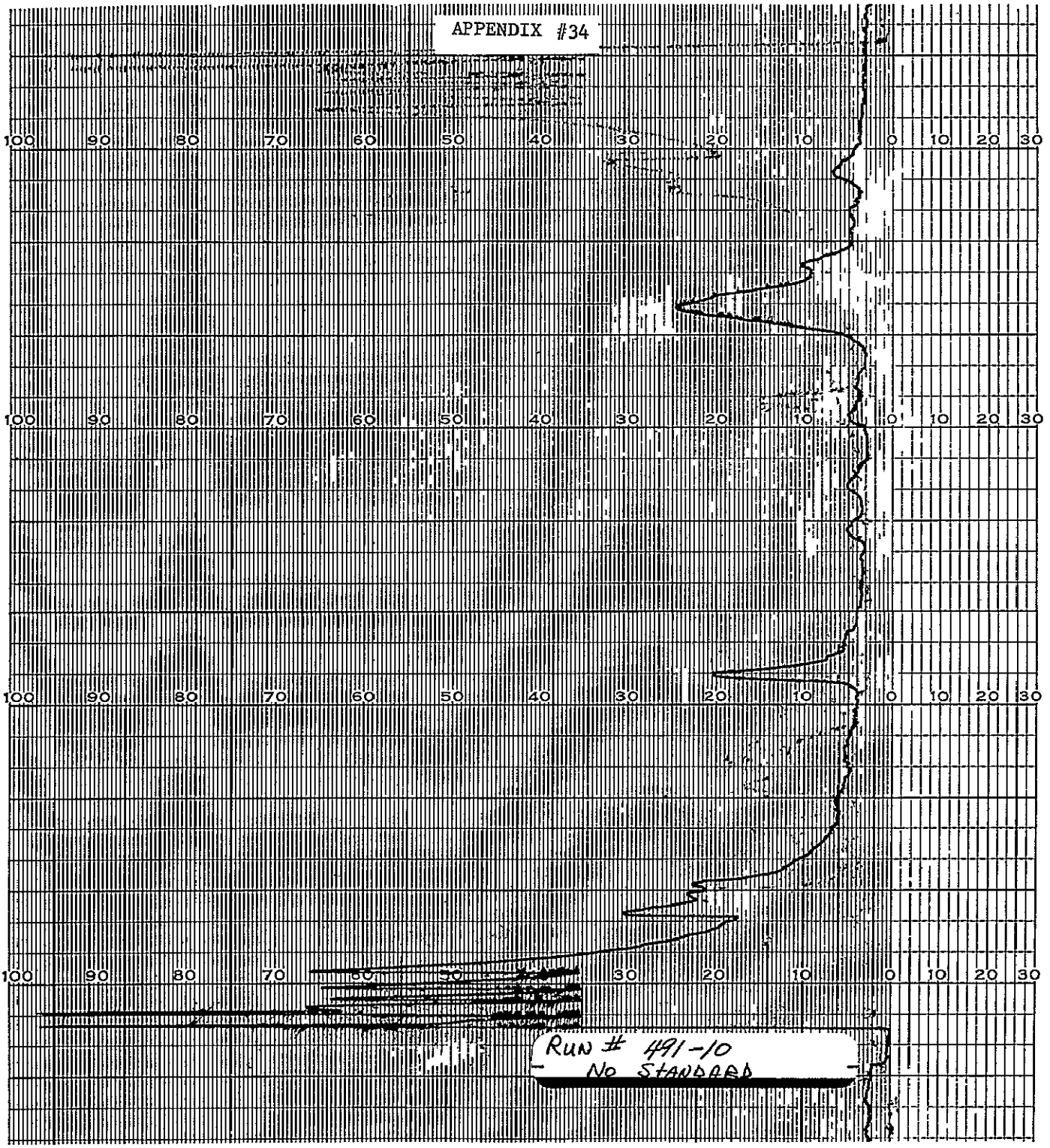

100 90 80 70 60 50 40 30 20 10 0 10 20 30
Run# 491-7
No Internal Standard

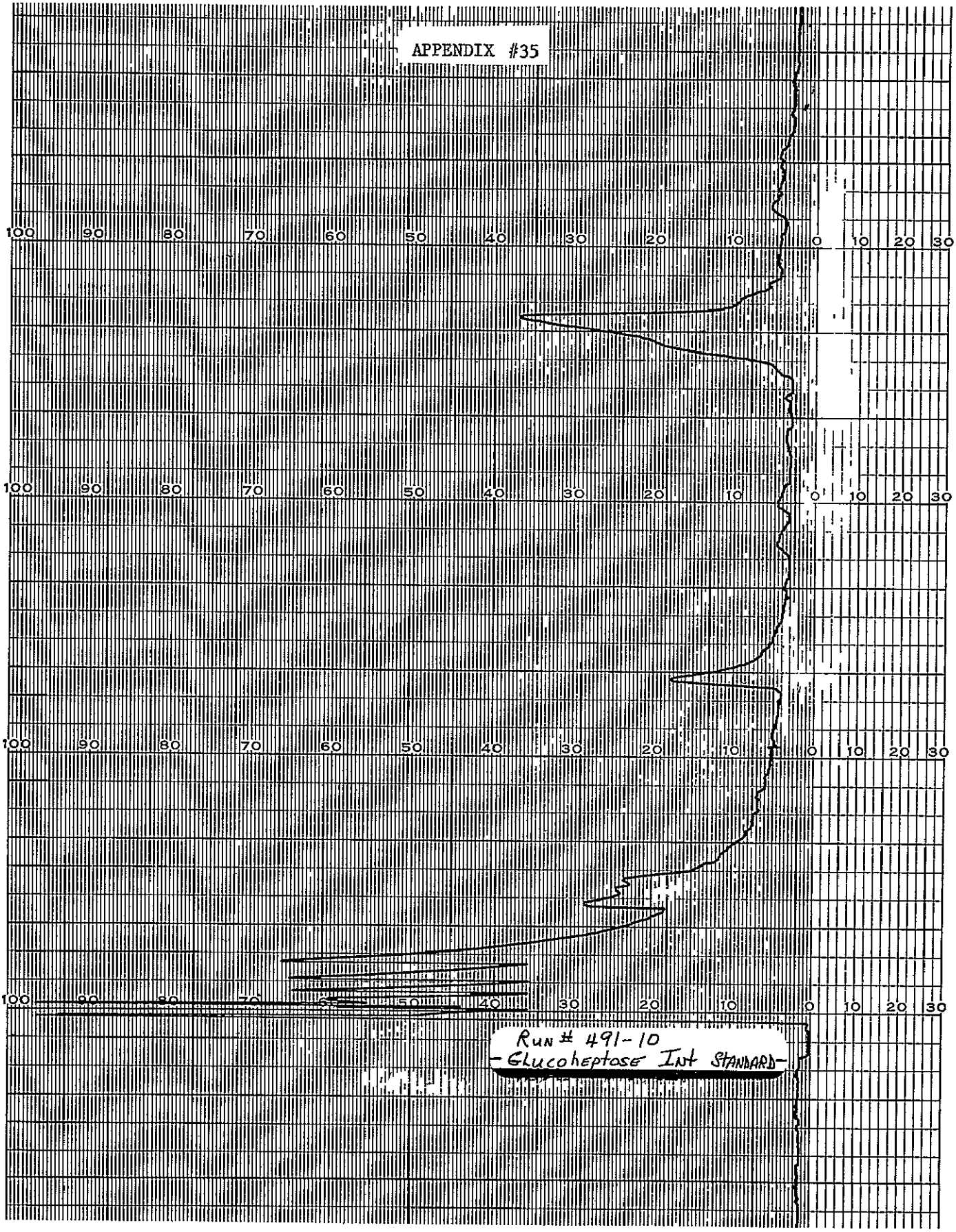
APPENDIX #31

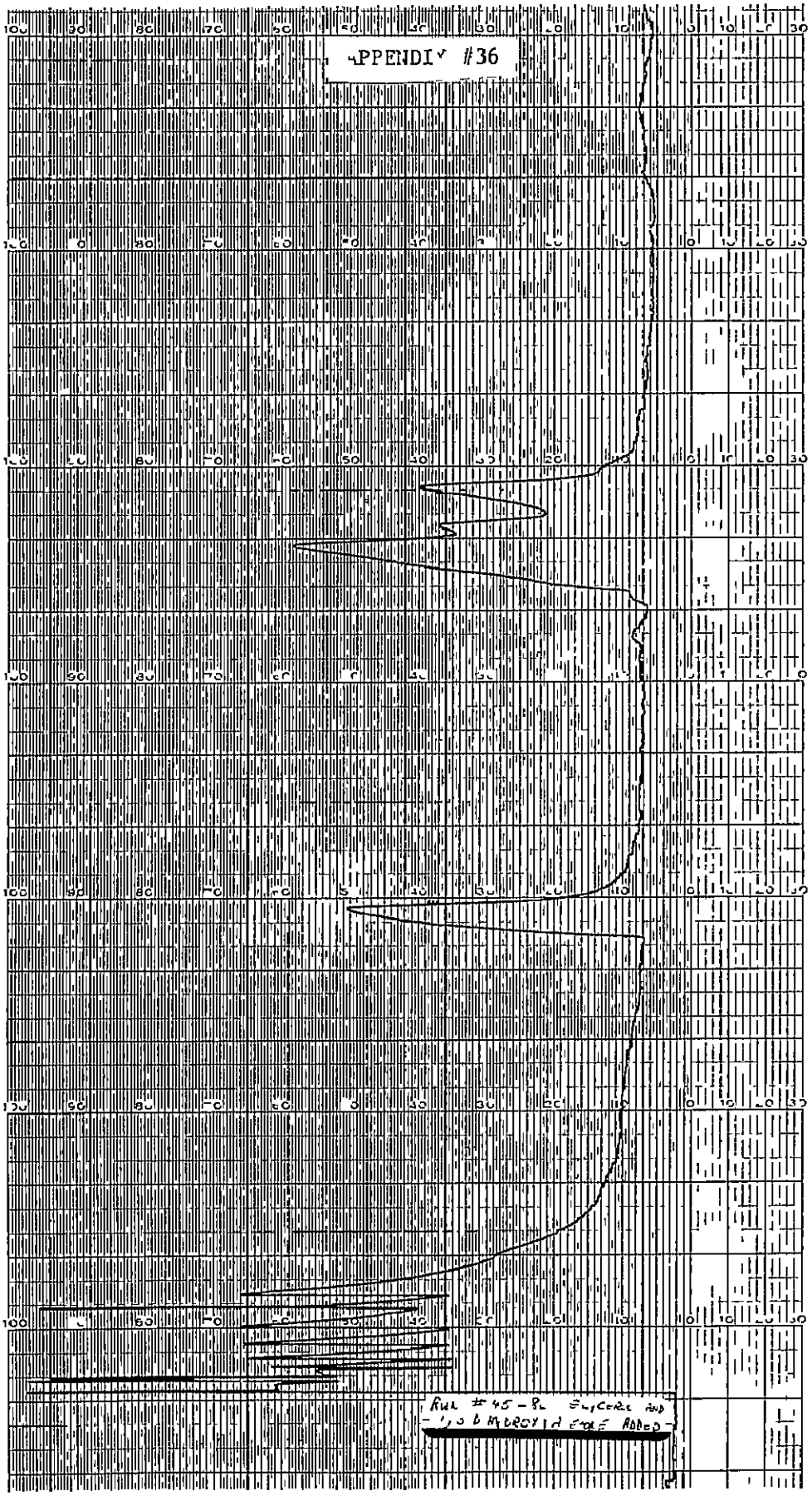

100 90 80 70 60 50 40 30 20 10 0 10 20 30
RUN # 491-7
- GLUCOHEPTOSE INT STANDARD


100
90
80
70
60
50
40
30
20
10
0
10
120
30

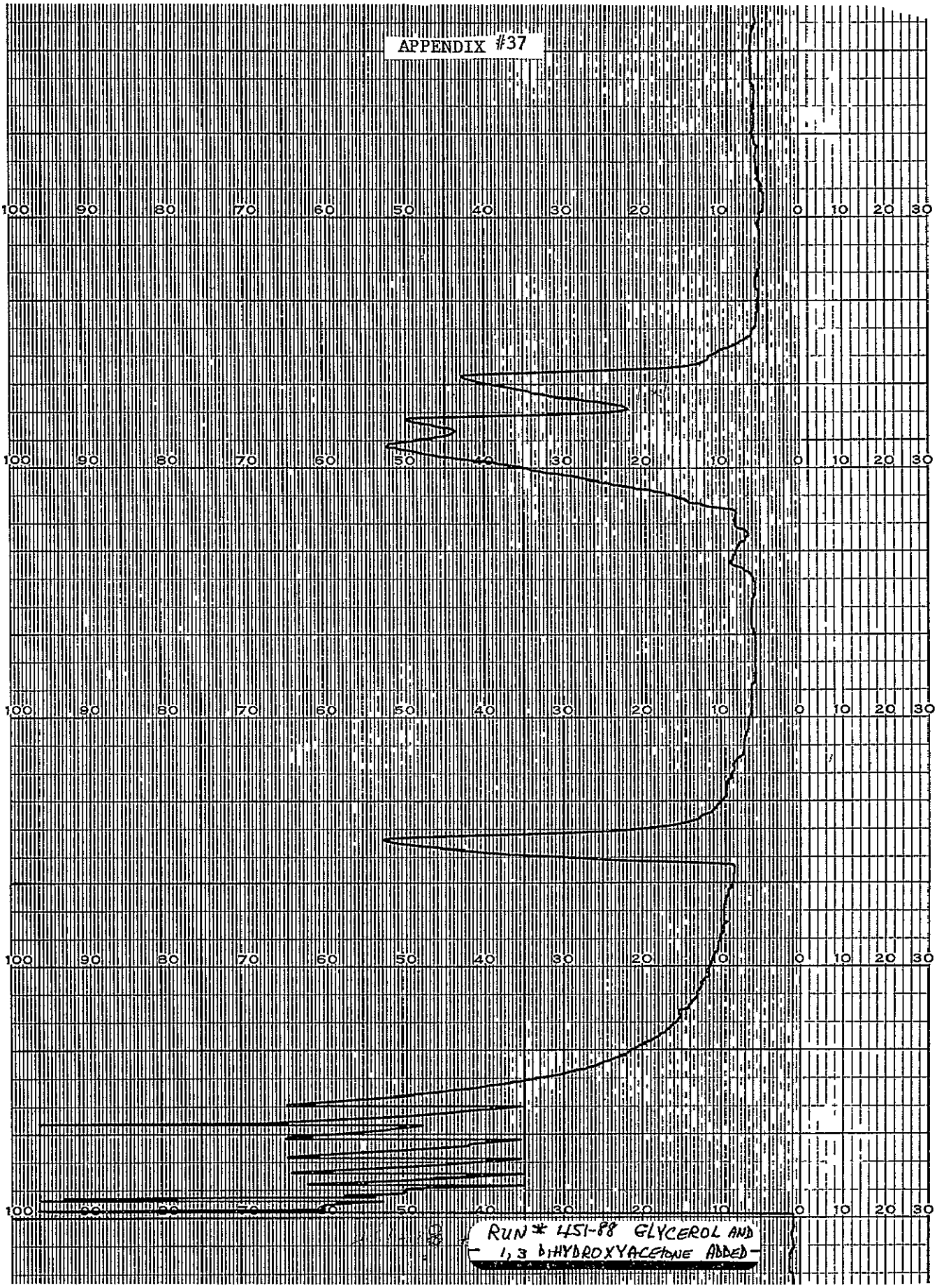

Run # 491-8
GLUCONEPTOSE INT SHANTOP


APPENDIX #34
100 90 80 70 60 50 40 30 20 10 0 10 20 30
100 90 80 70 60 50 40 30 20 10 0 10 20 30
100 90 80 70 60 50 40 30 20 10 0 10 20 30
100 90 80 70 60 50 40 30 20 10 0 10 20 30
Run # 491-10
No STANDARD

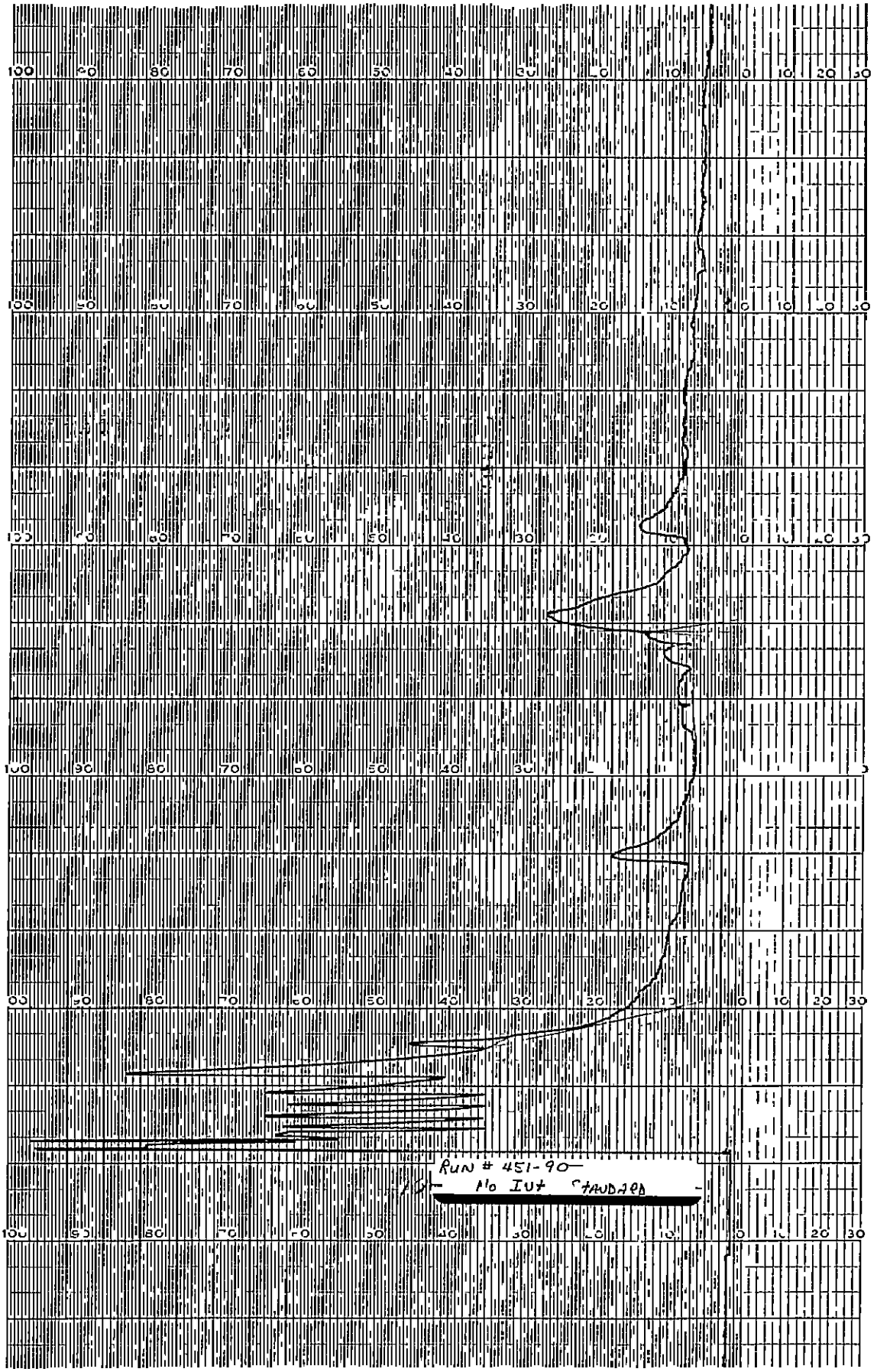

APPENDIX #35
100 90 80 70 60 50 40 30 20 10 0 10 20 30
100 90 80 70 60 50 40 30 20 10 0 10 20 30
100 90 80 70 60 50 40 30 20 10 0 10 20 30
100 90 80 70 60 50 40 30 20 10 0 10 20 30
RUN # 491-10
-GLUCOHEPTOSE INT STANDARD-


APPENDIX #36
Run #45-B Glycerol and
1,3 Hydroxyl Ester Added

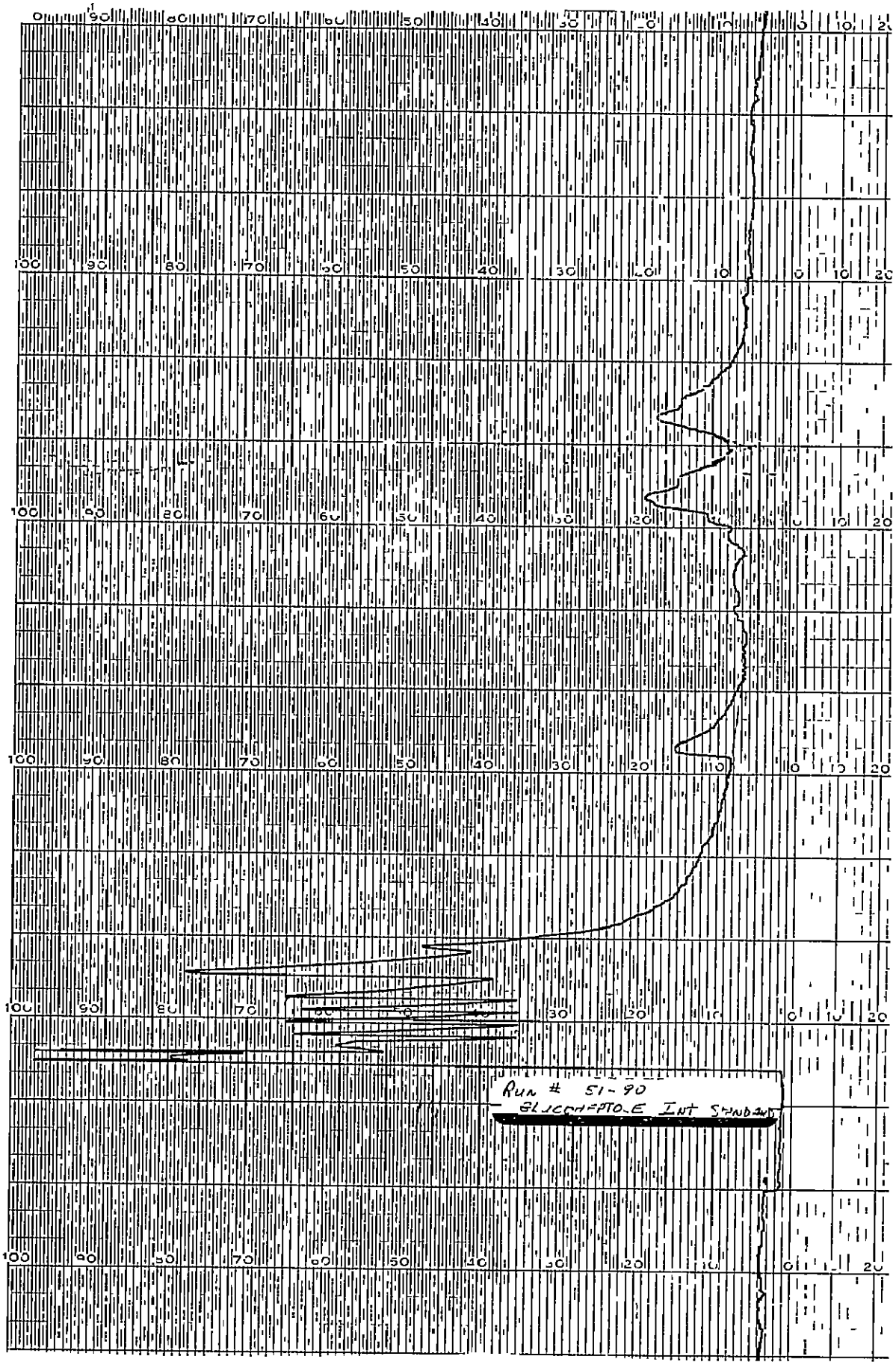
APPENDIX #37


100 90 80 70 60 50 40 30 20 10 0 10 20 30
RUN # 451-88 GLYCEROL AND
1, 3 DIHYDROXYACETONE ADDED

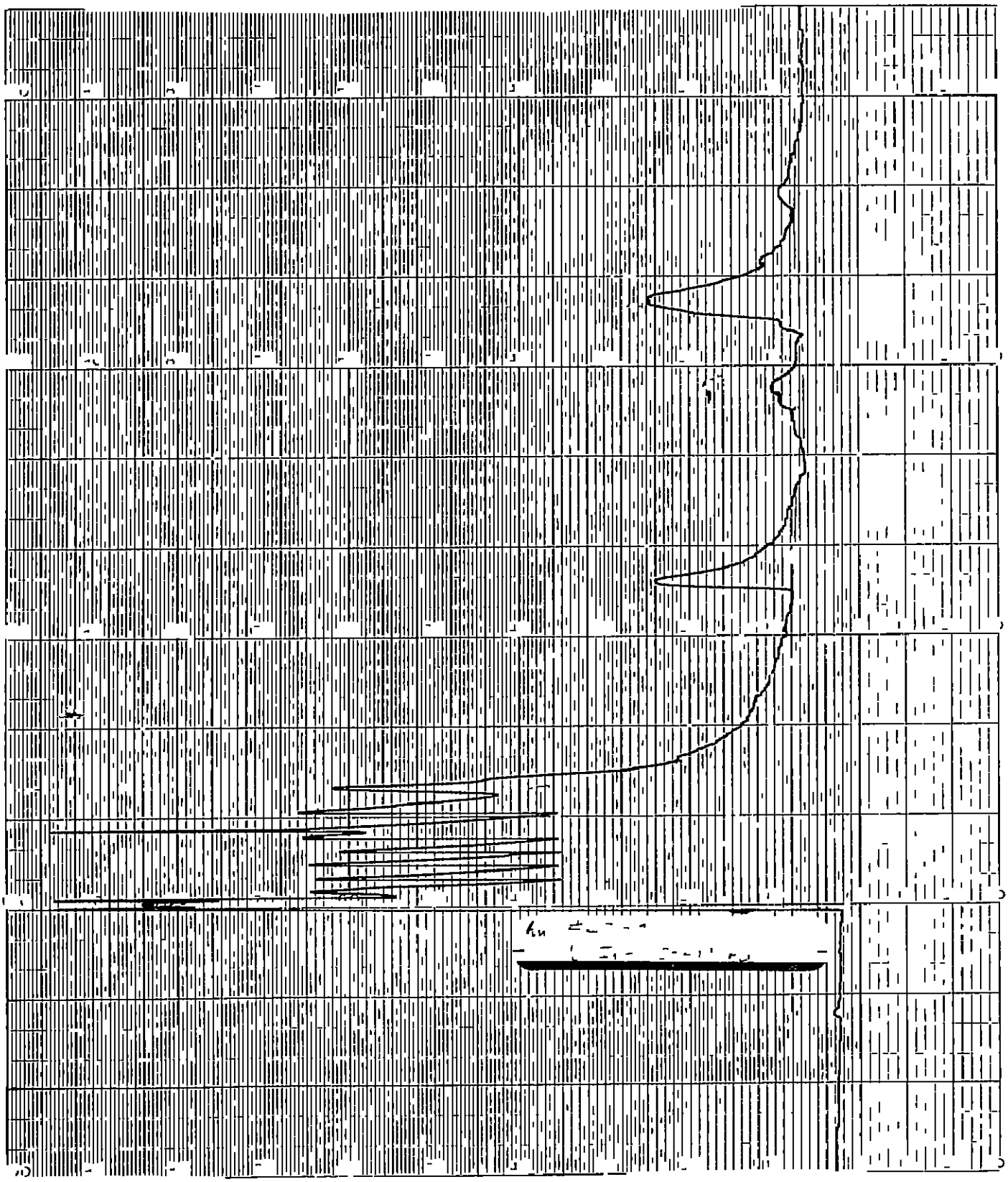
APPENDIX 38



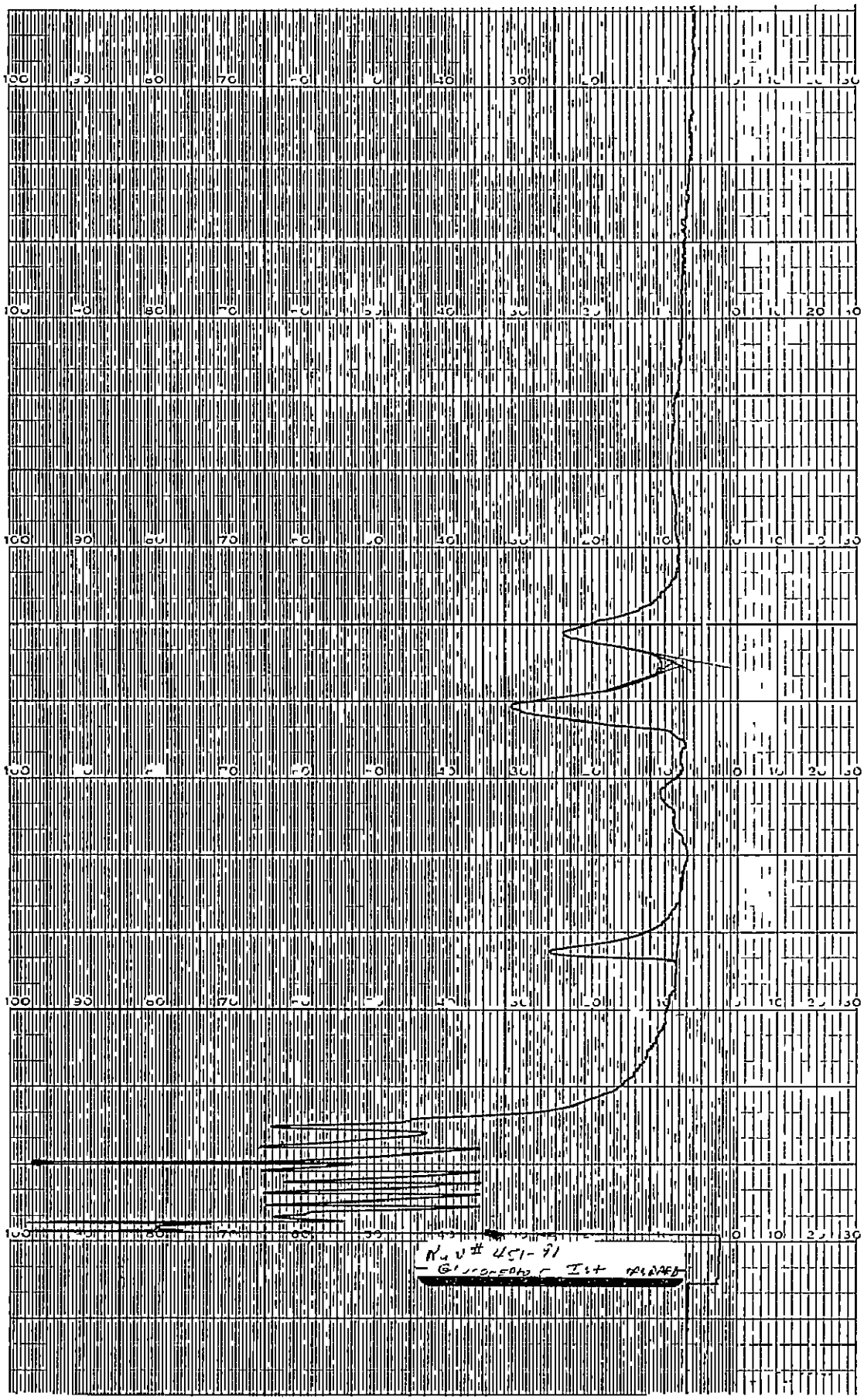
APPENDIX 39



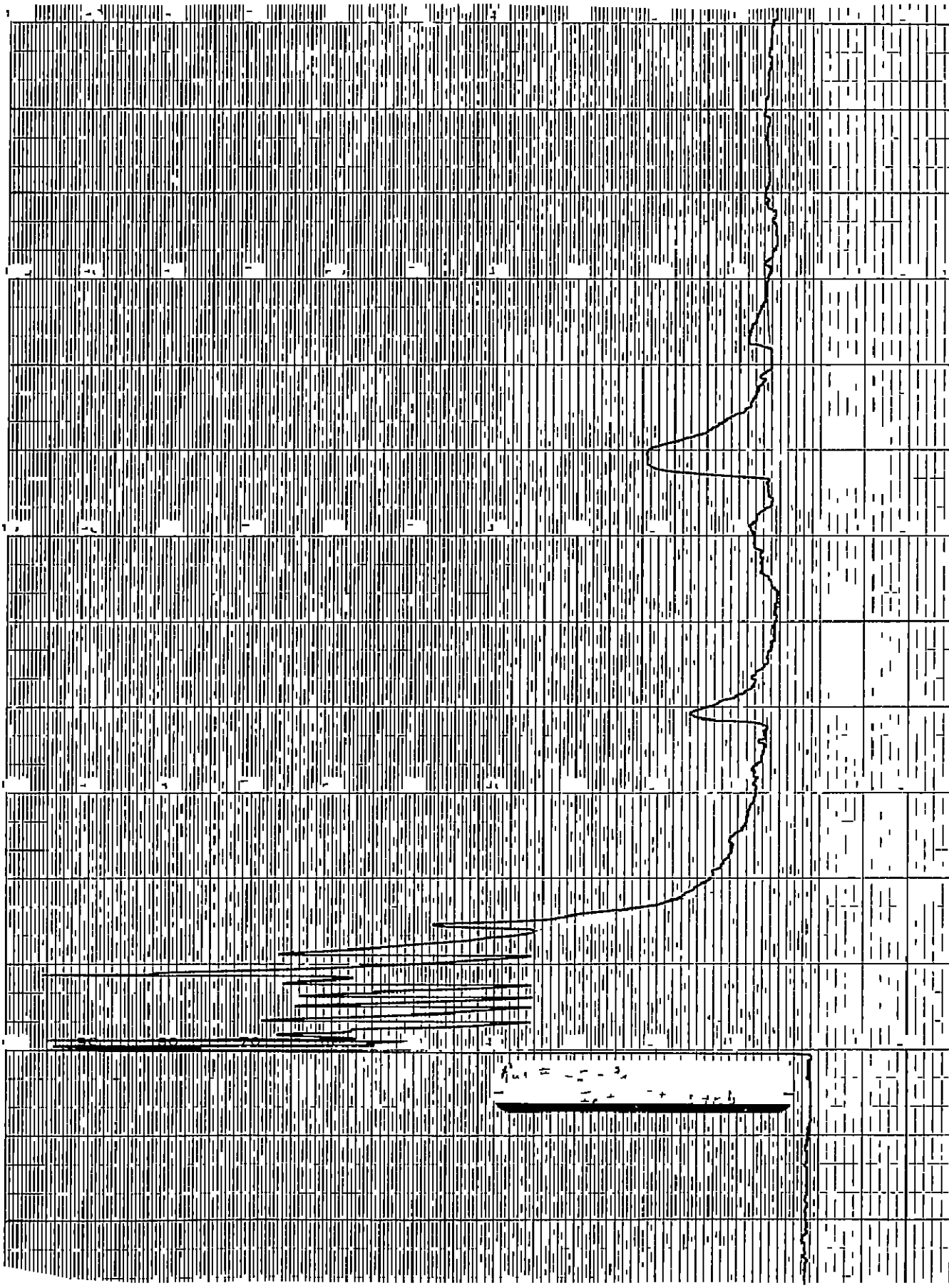
APPENDIX 40



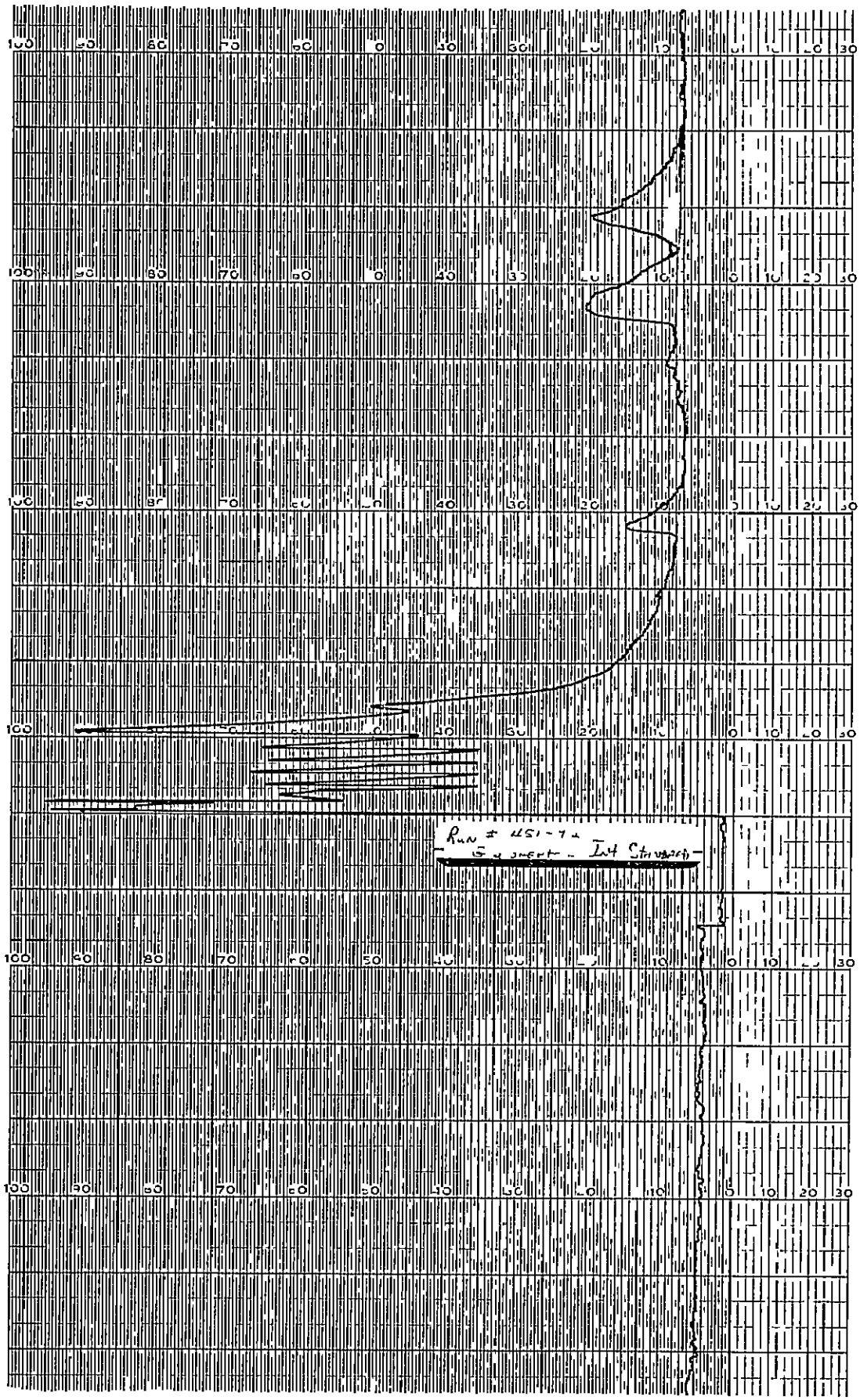
APPENDIX 41



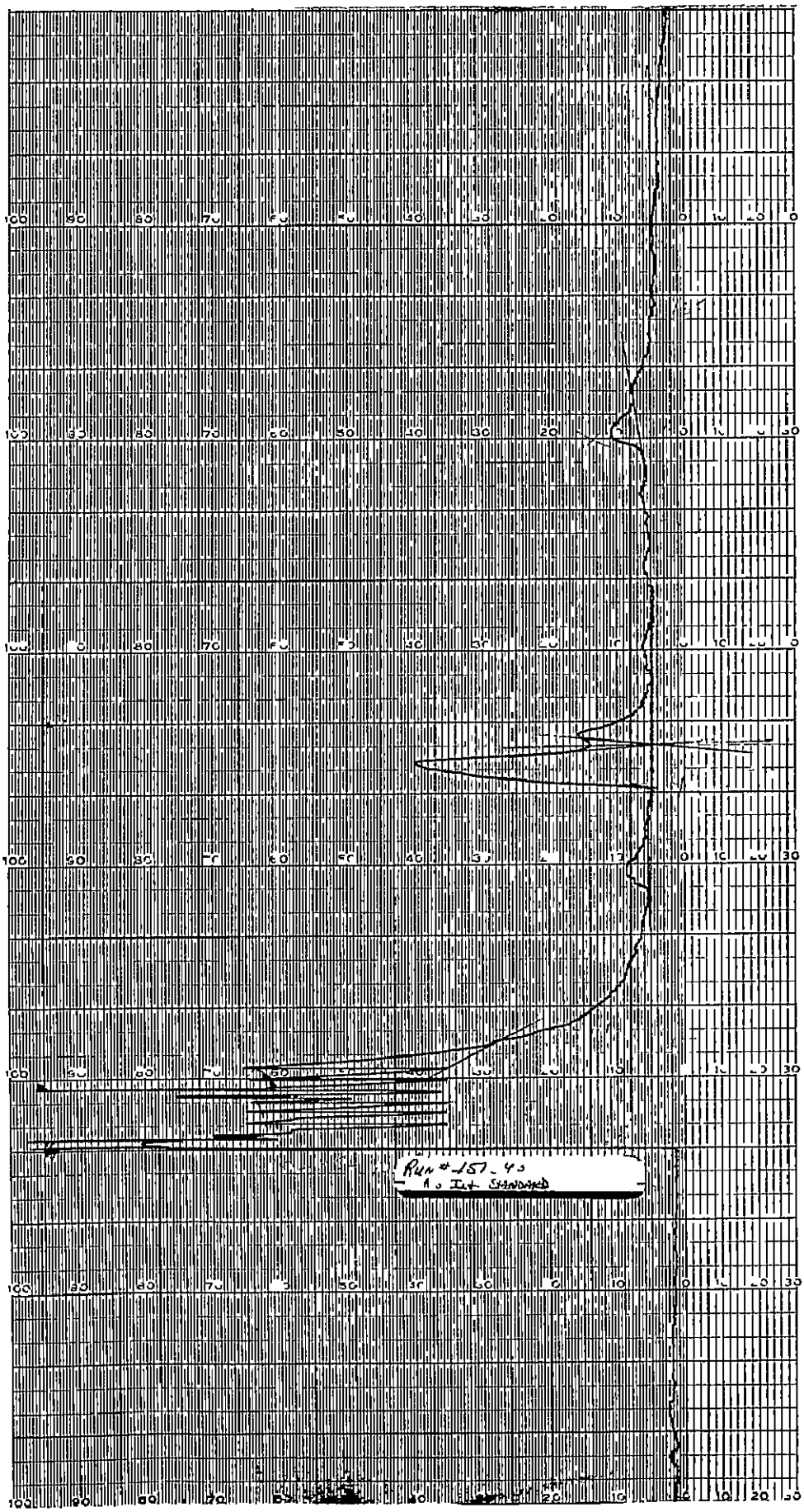
APPENDIX 42



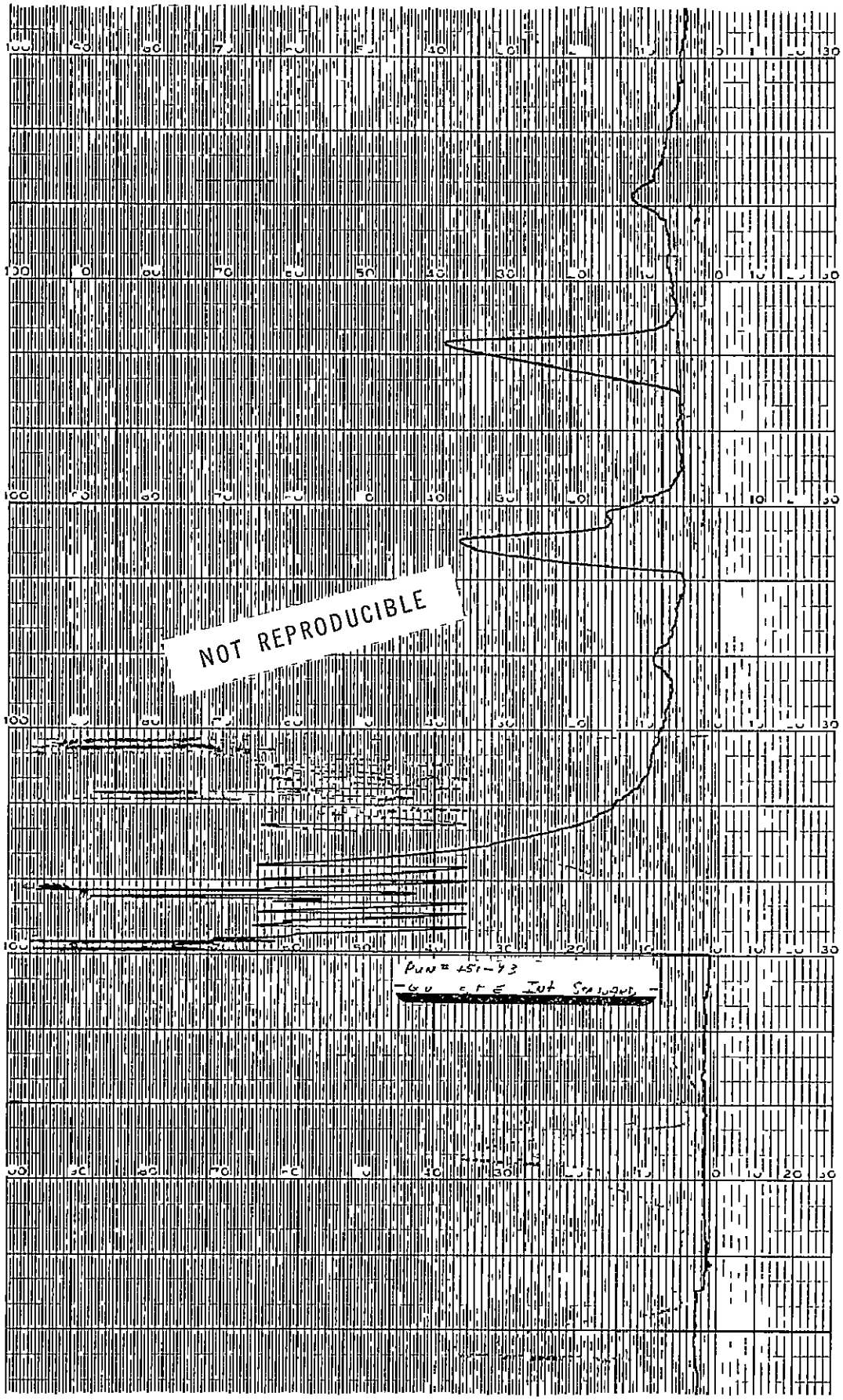
APPENDIX 43



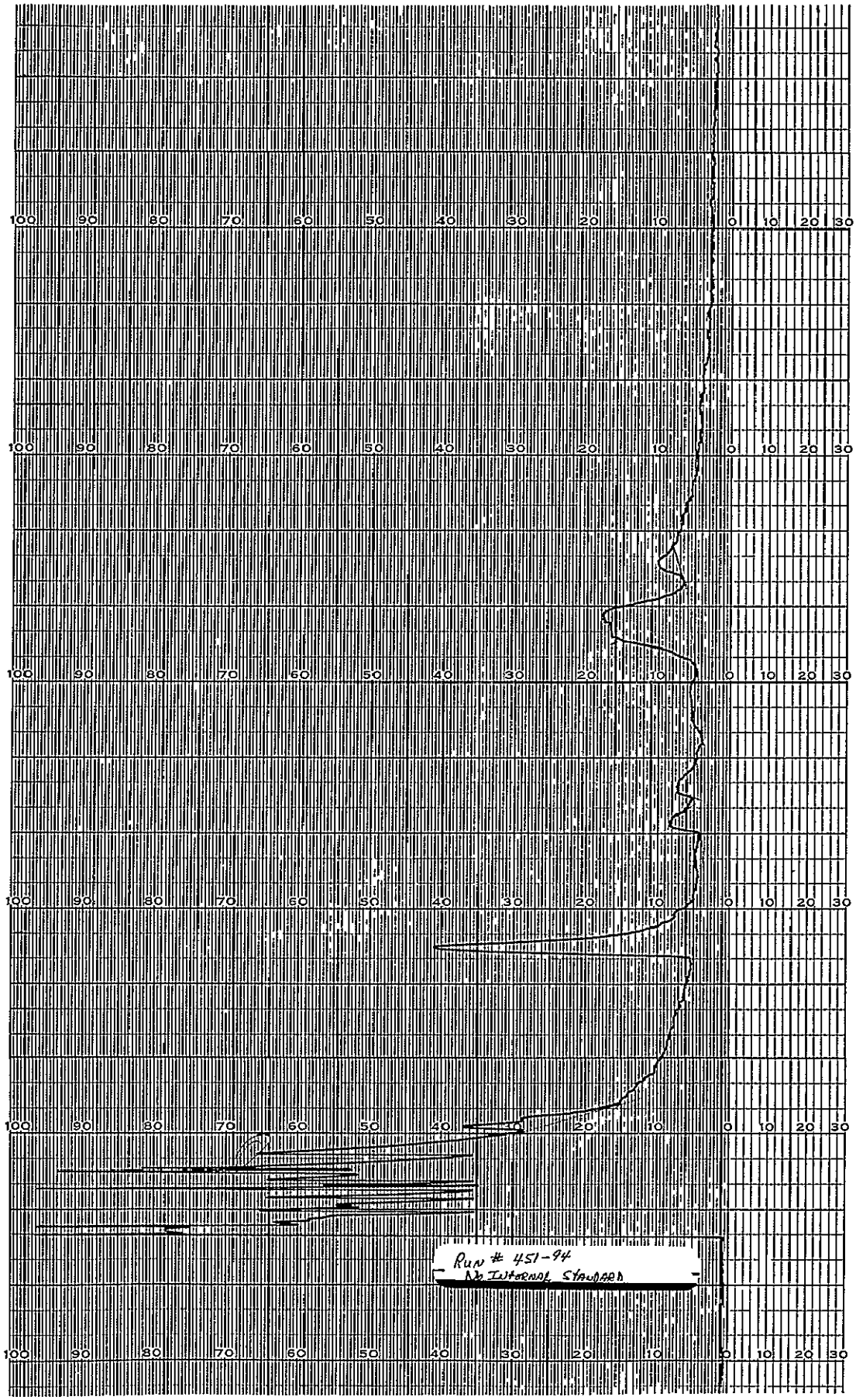
APPENDIX 44



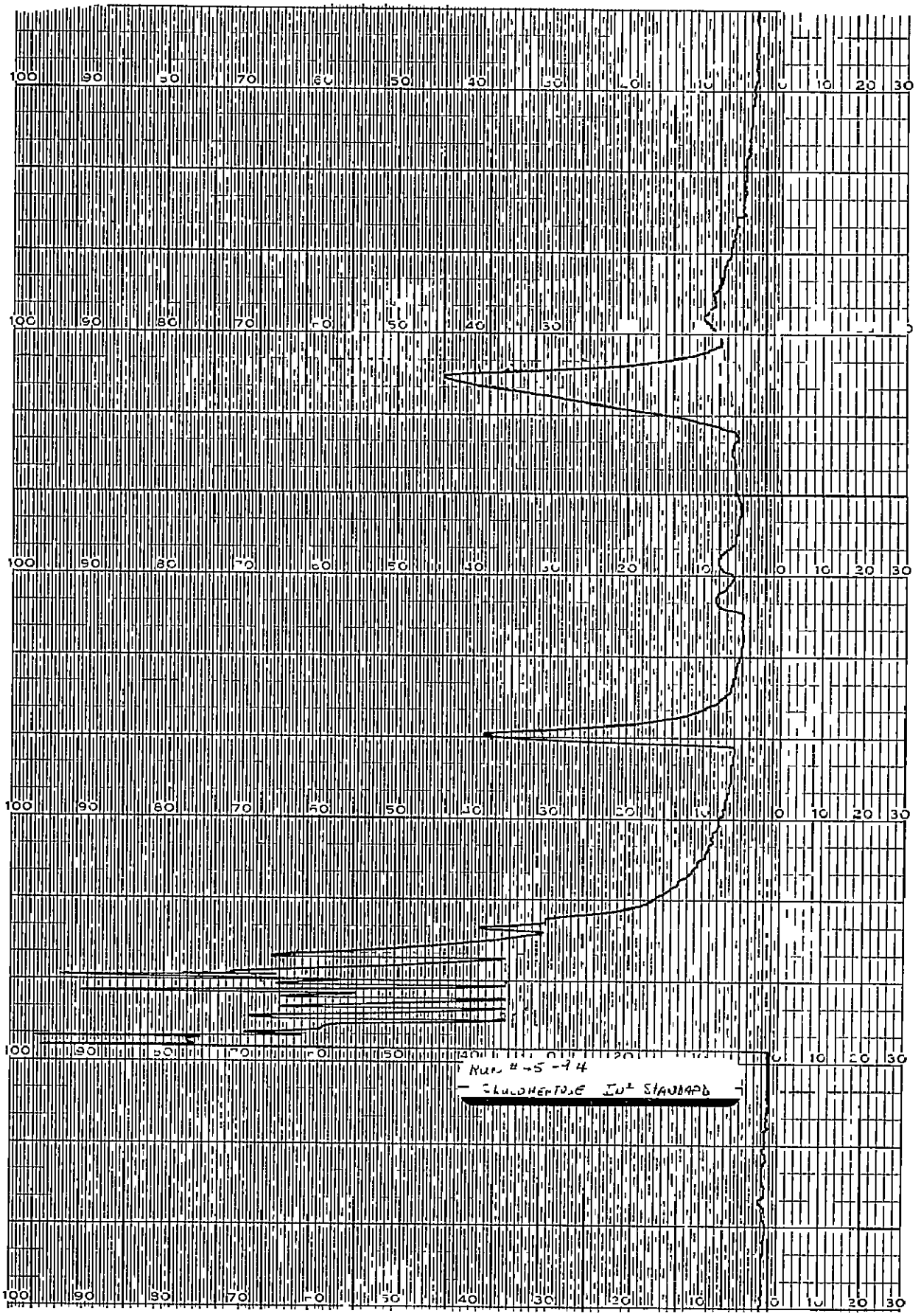
APPENDIX 45



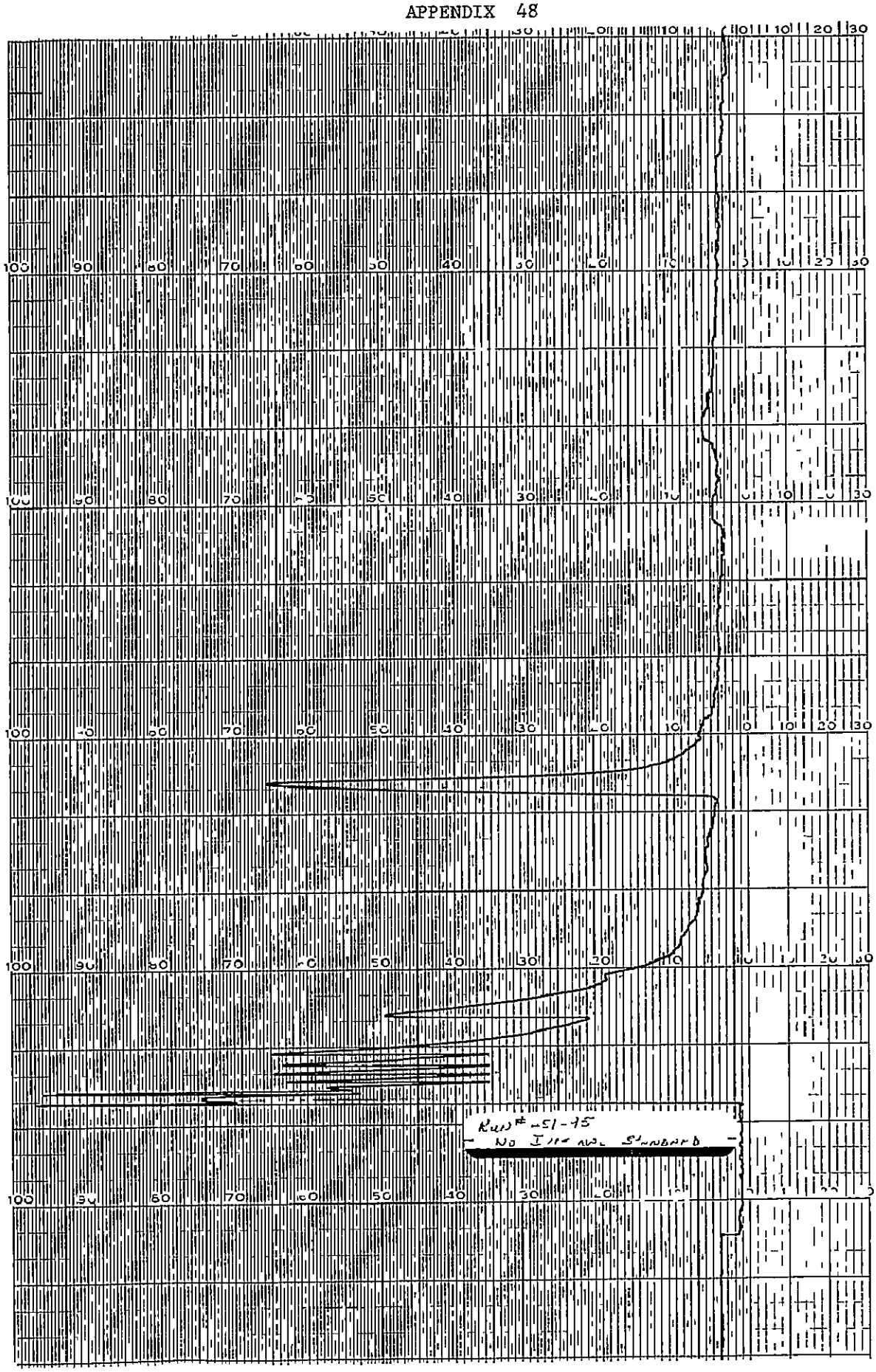
APPENDIX 46


100 90 80 70 60 50 40 30 20 10 0 10 20 30
Run # 451-94
No Internal Standard

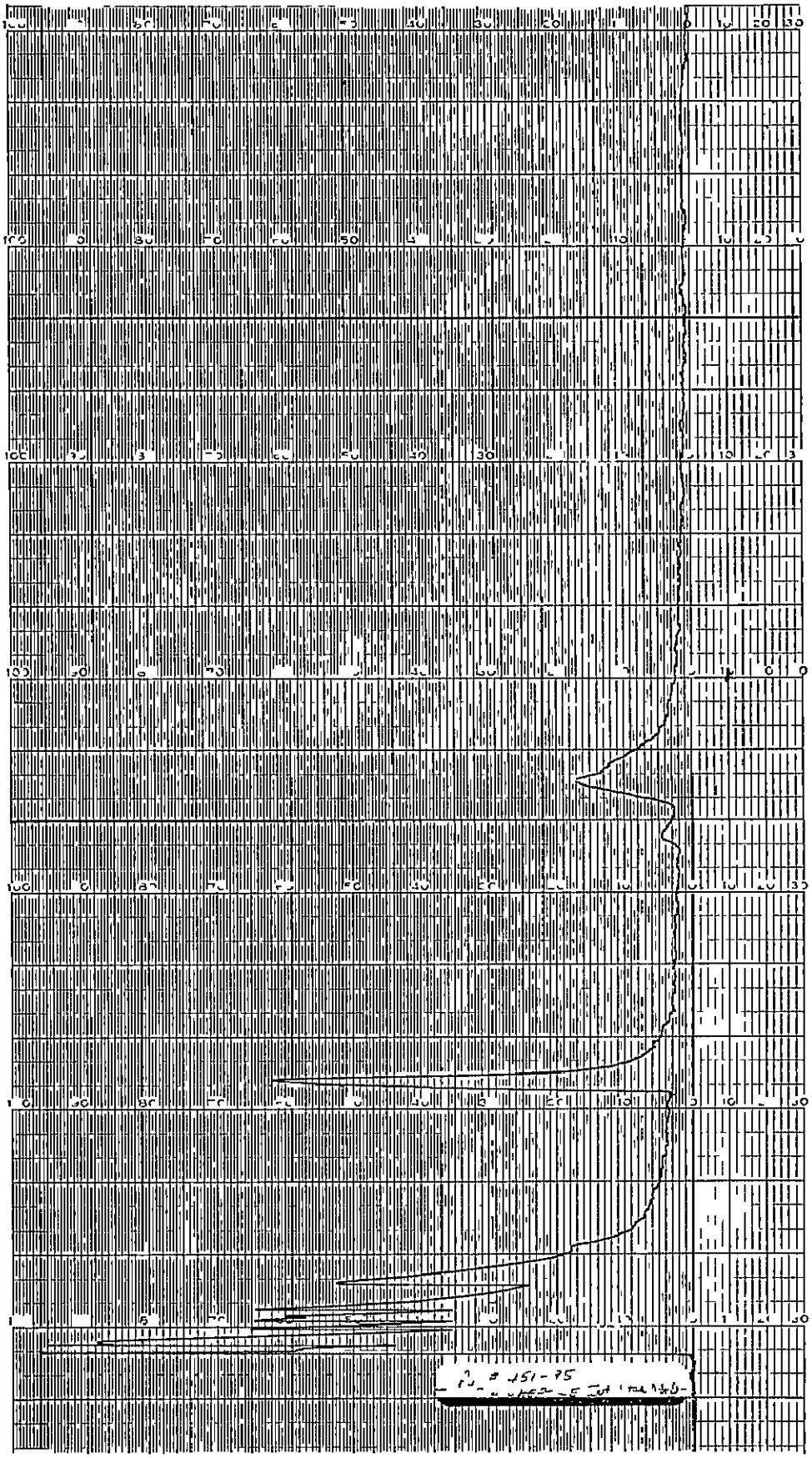
APPENDIX 47



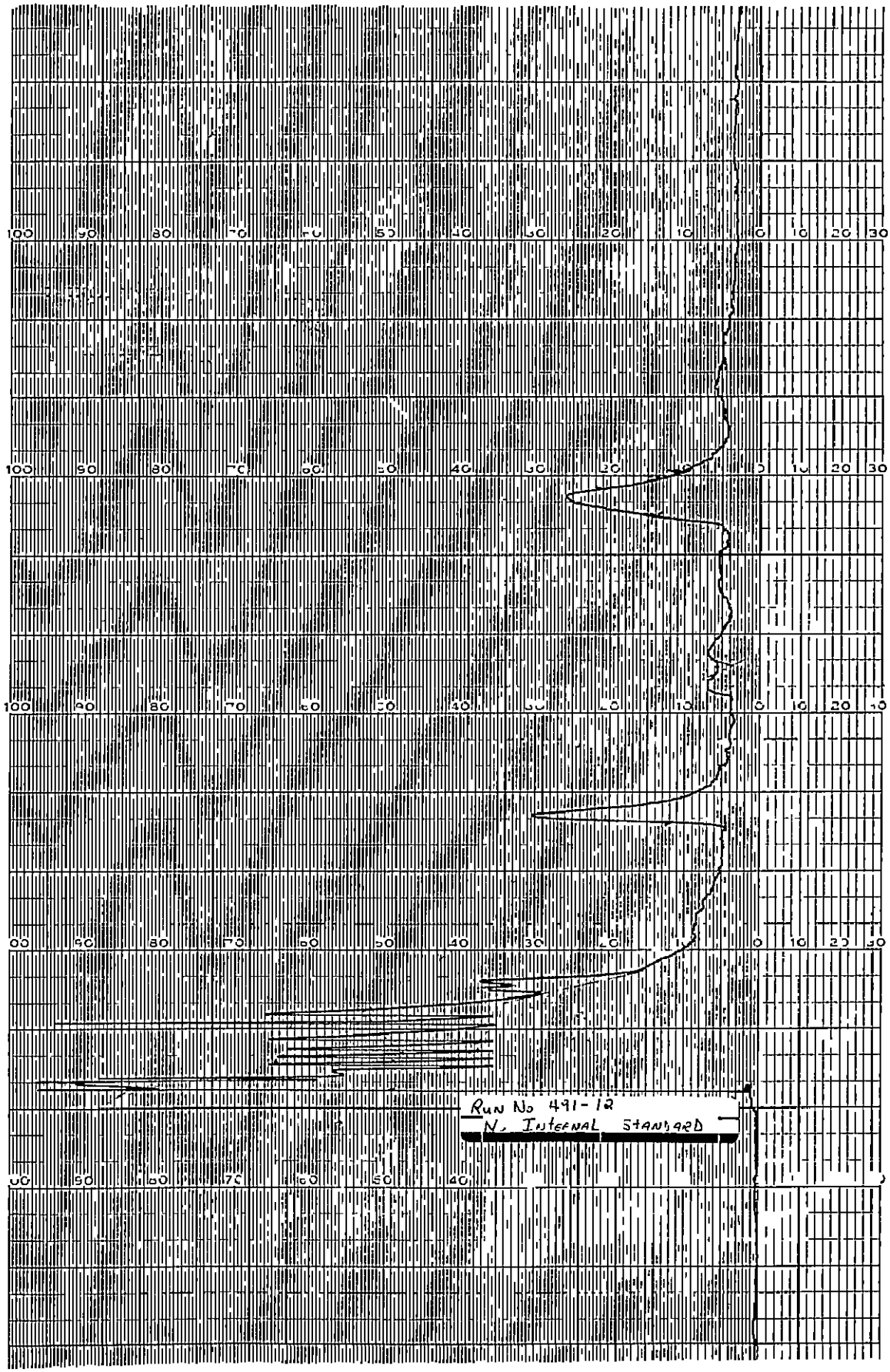
APPENDIX 48



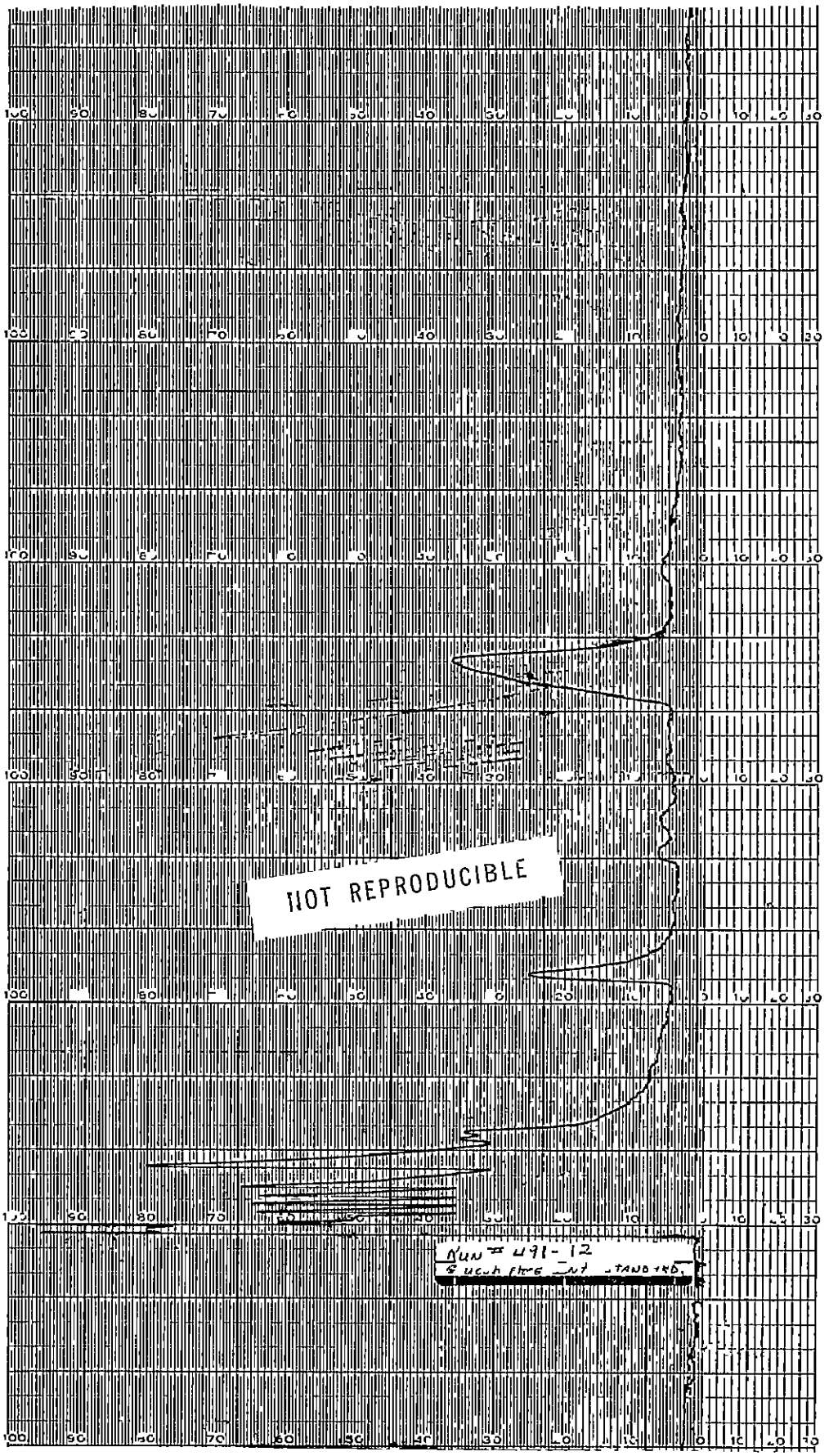
APPENDIX 49



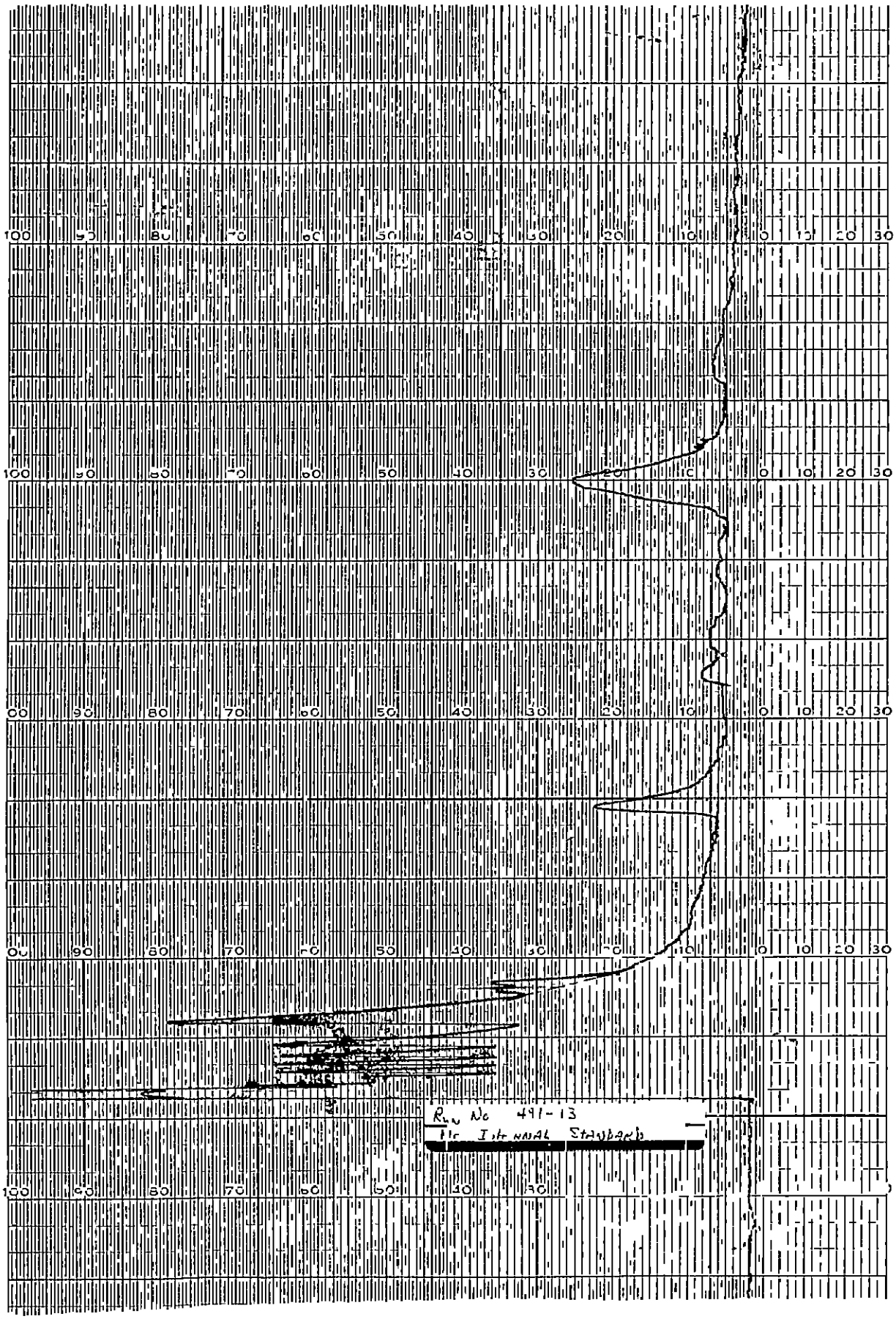
APPENDIX 50



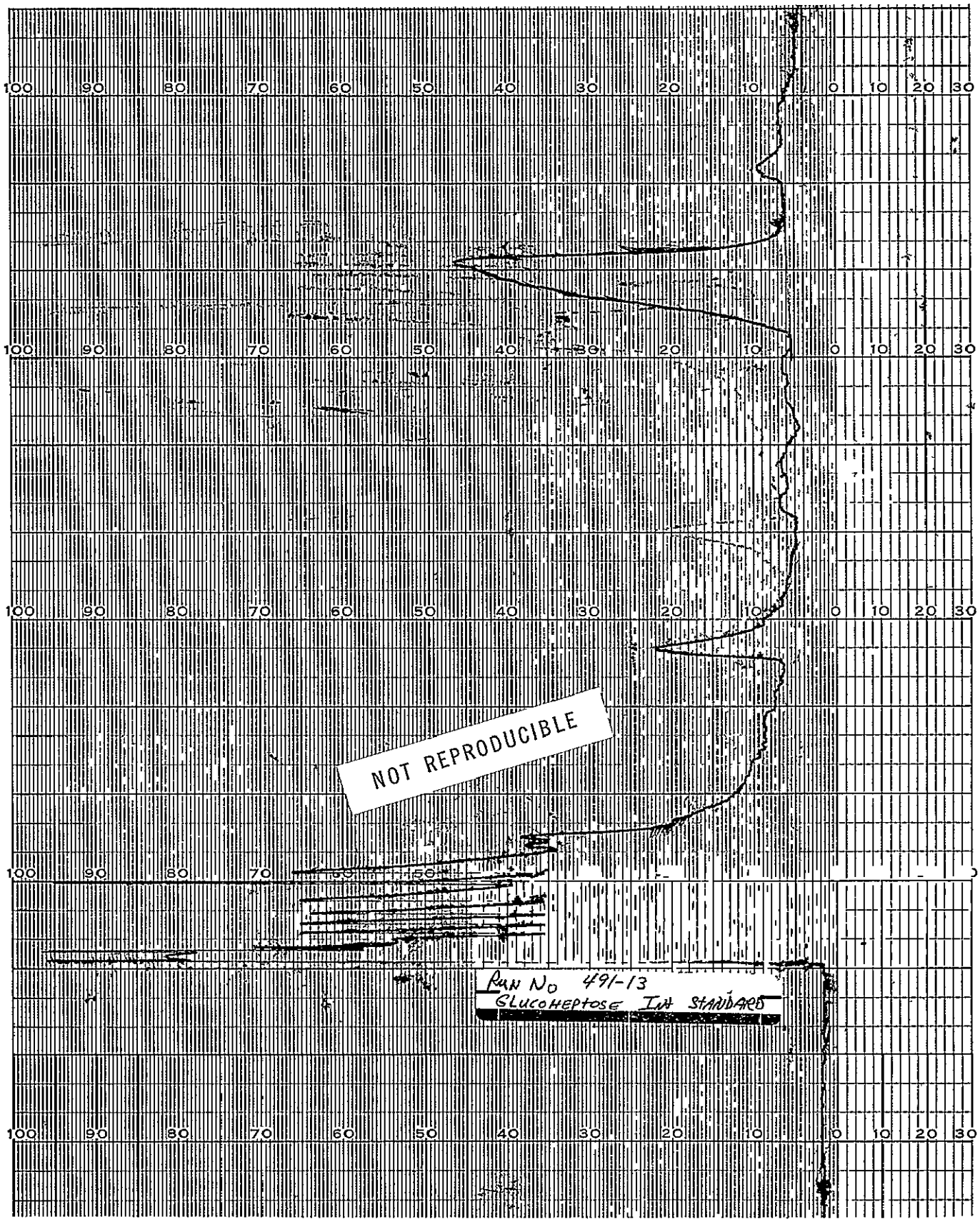
APPENDIX 51



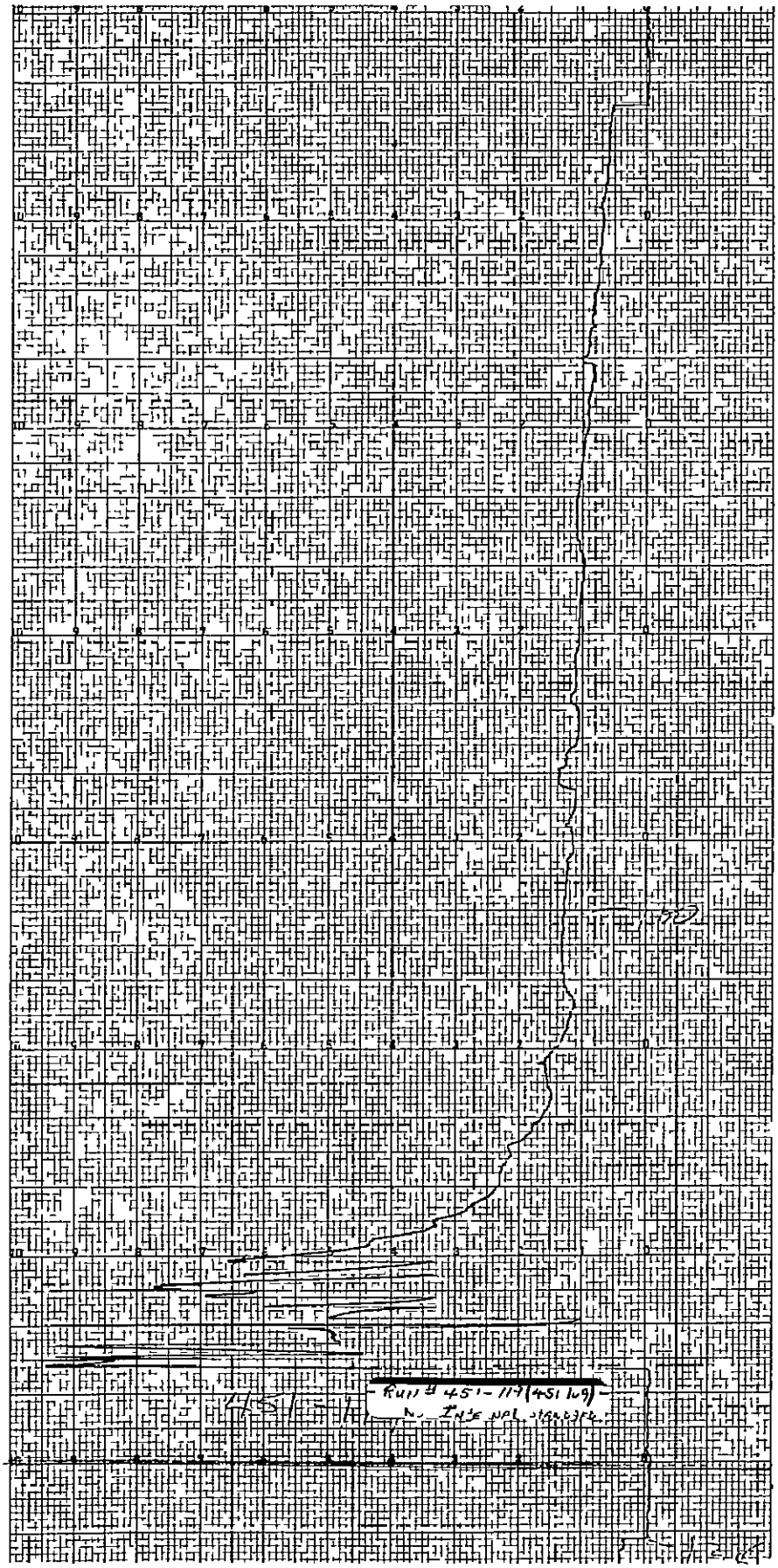
APPENDIX 52



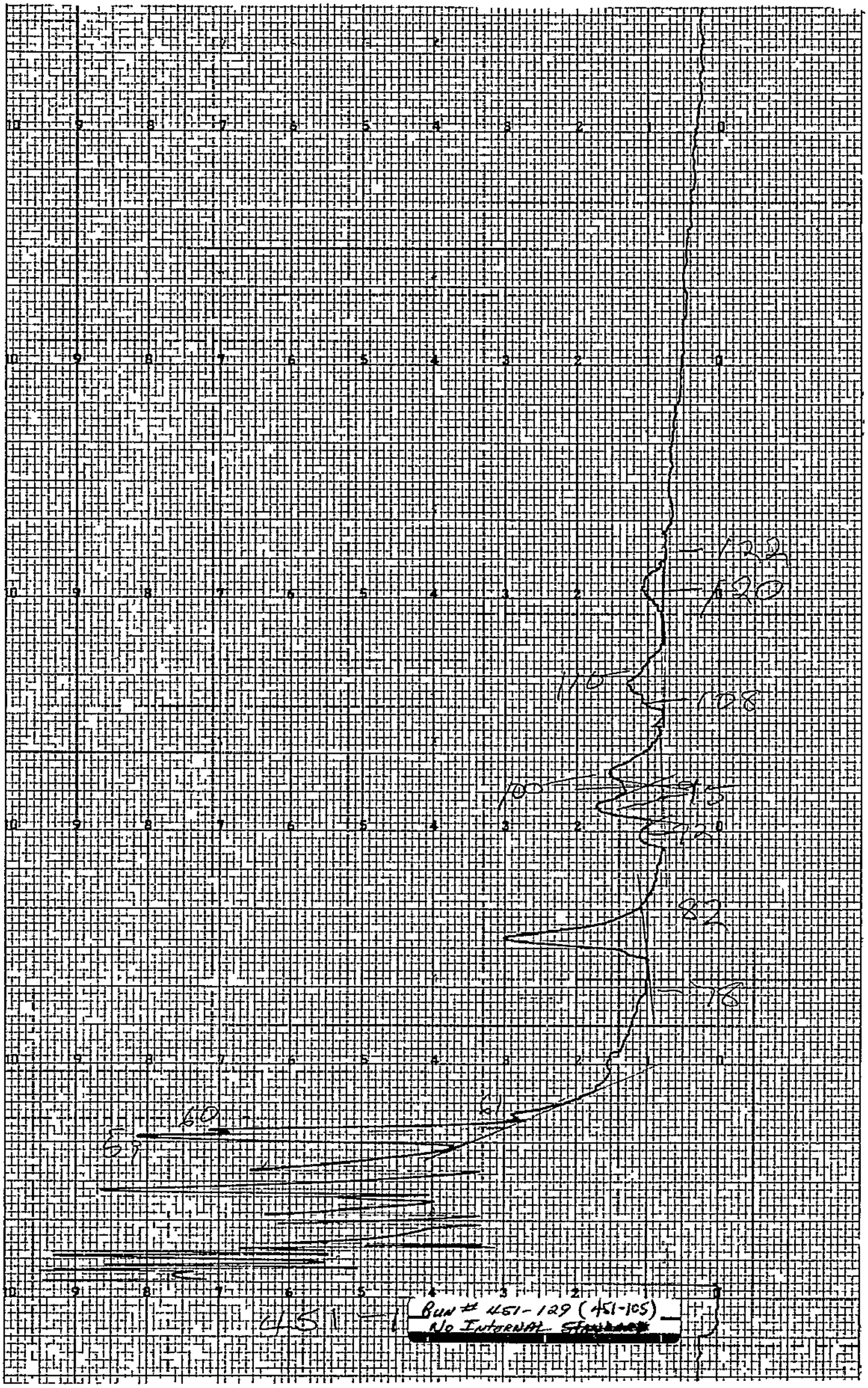
APPENDIX 53


100 90 80 70 60 50 40 30 20 10 0 10 20 30
100 90 80 70 60 50 40 30 20 10 0 10 20 30
100 90 80 70 60 50 40 30 20 10 0 10 20 30
100 90 80 70 60 50 40 30 20 10 0 10 20 30
100 90 80 70 60 50 40 30 20 10 0 10 20 30
NOT REPRODUCIBLE
RUN NO 491-13
GLUCOHEPTOSE IN STANDARDS

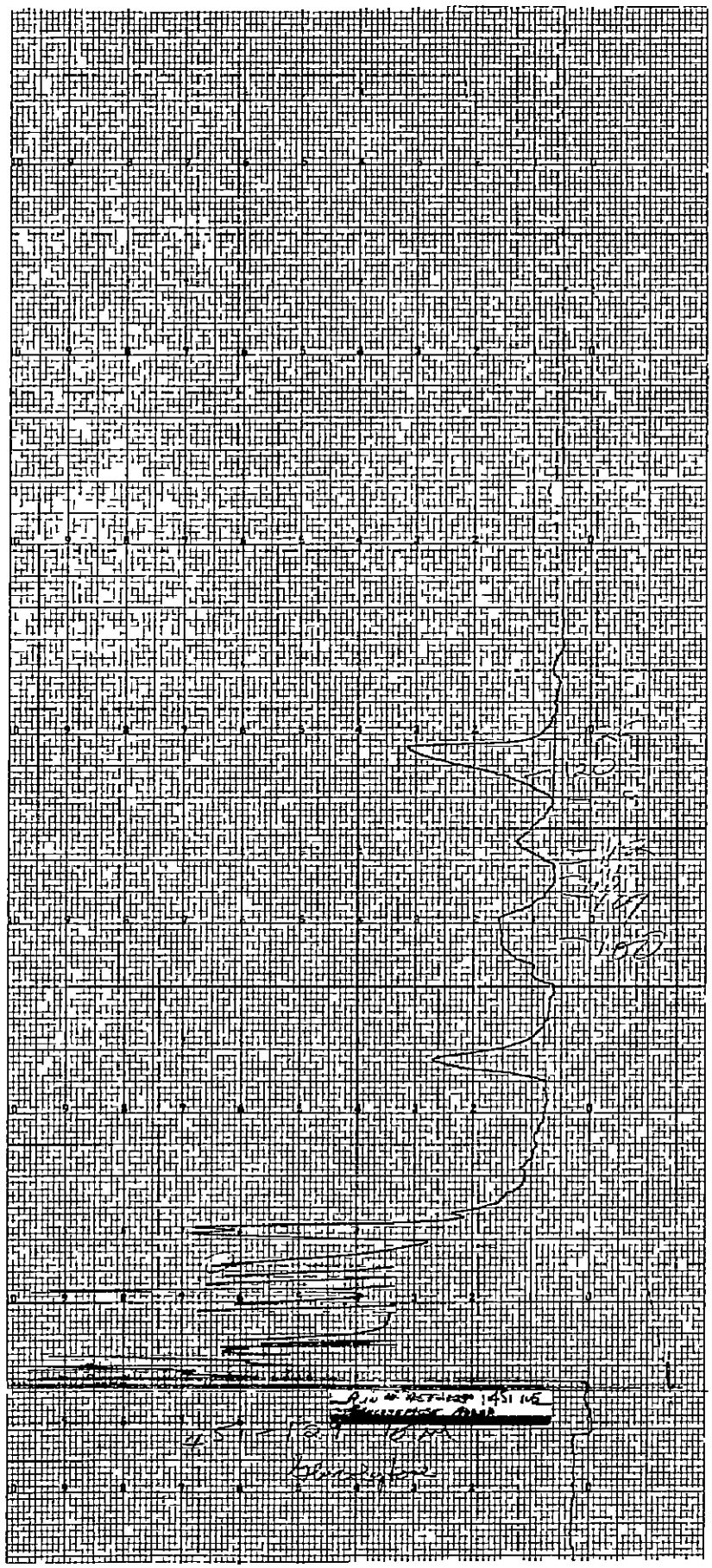
APPENDIX 54



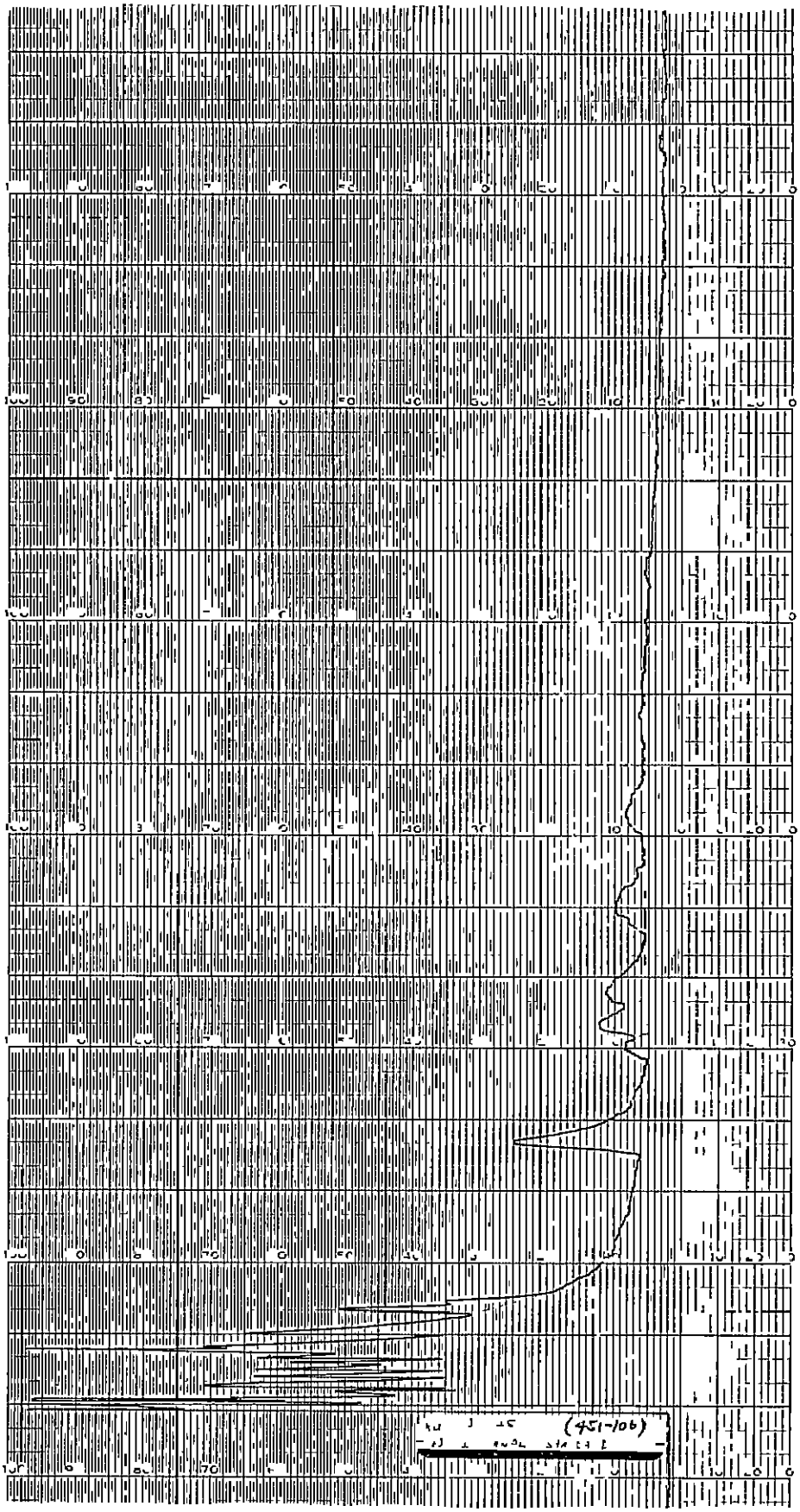
APPENDIX 55


122
120
110
108
100
95
92
82
78
61
60
451-1
RUN # 451-129 (451-105)
NO INTERNAL

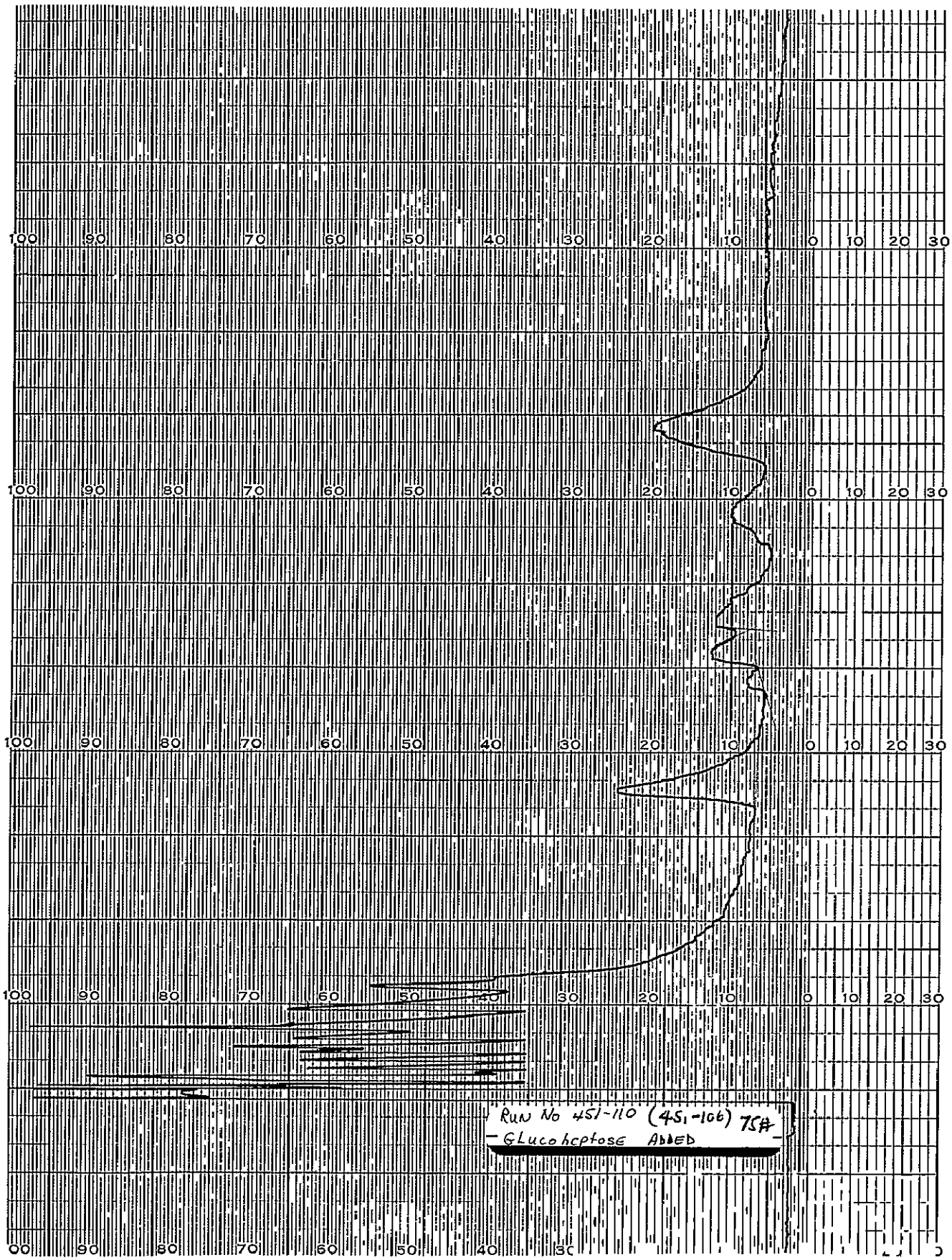
APPENDIX 56



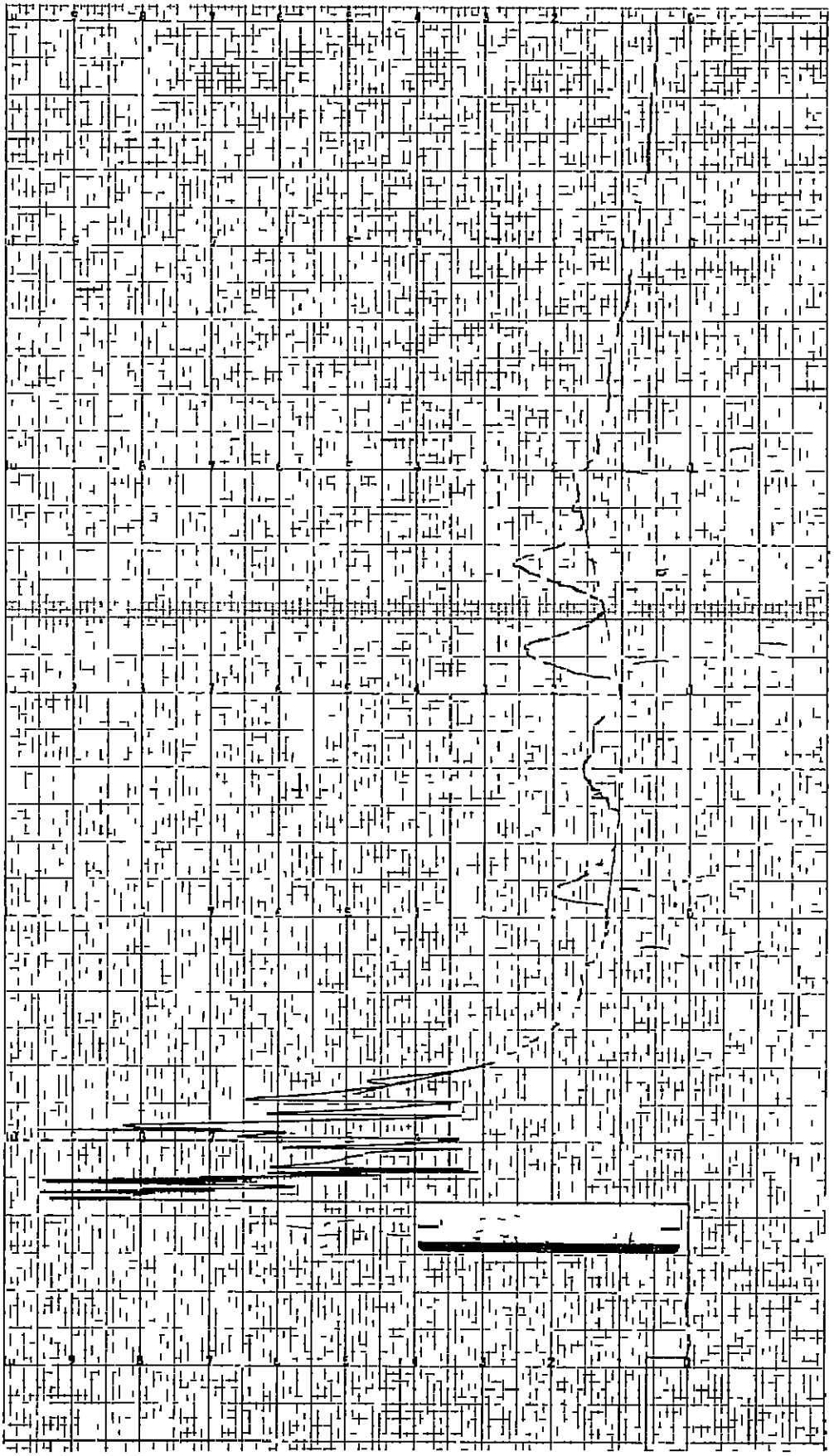
APPENDIX 57



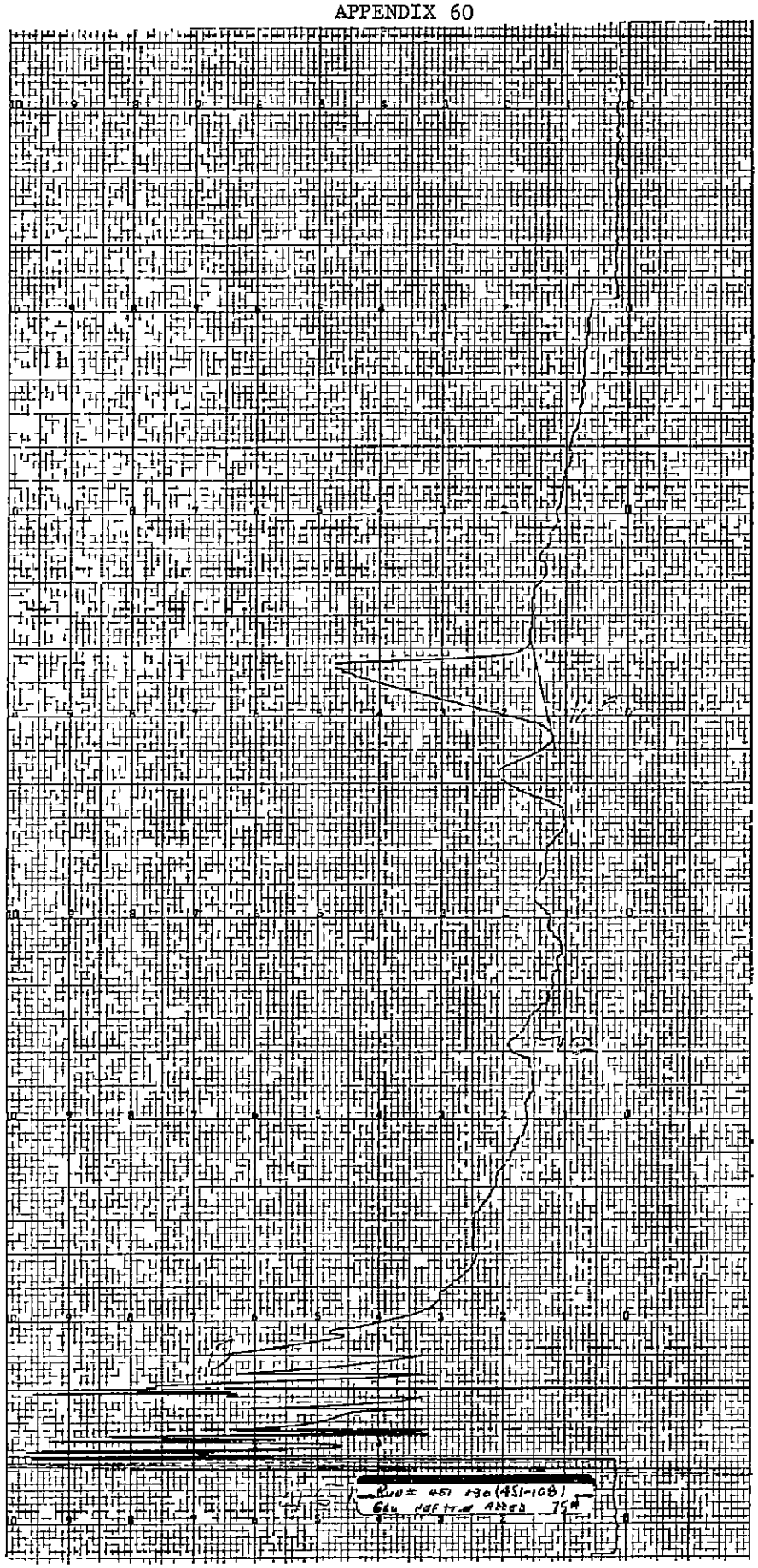
APPENDIX 58


100 90 80 70 60 50 40 30 20 10 0 10 20 30
100 90 80 70 60 50 40 30 20 10 0 10 20 30
100 90 80 70 60 50 40 30 20 10 0 10 20 30
100 90 80 70 60 50 40 30 20 10 0 10 20 30
RUN No 451-110 (45,-106) 75#
GLUCOHEPTOSE ADDED

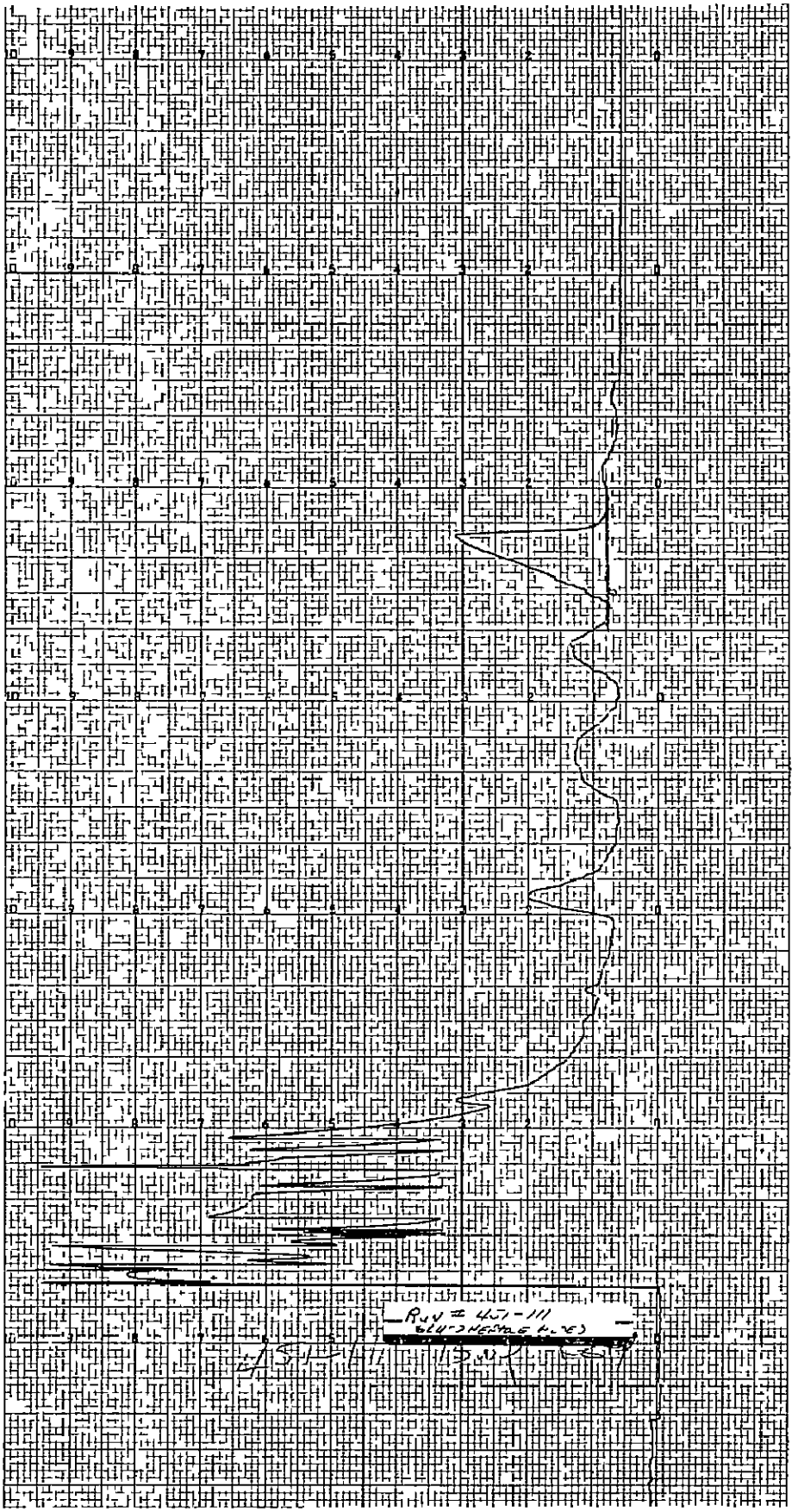
APPENDIX 59



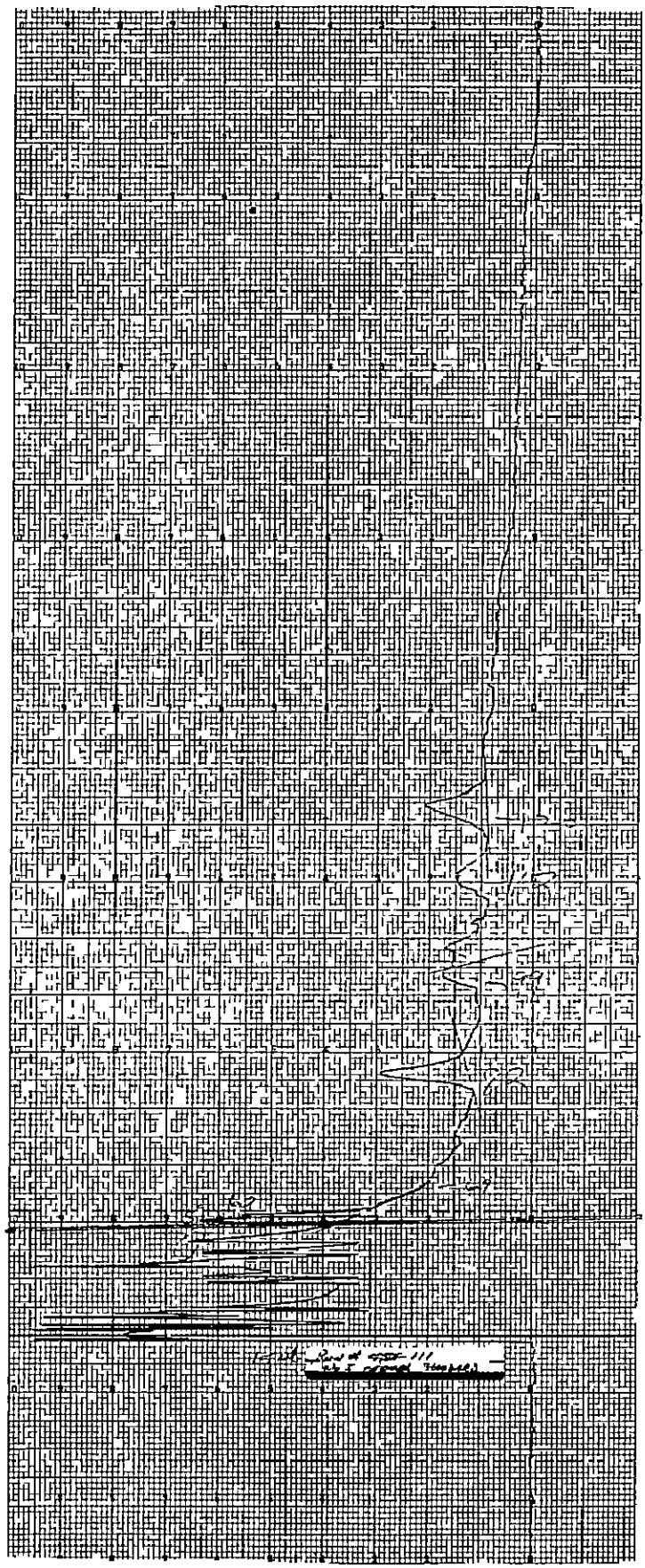
APPENDIX 60



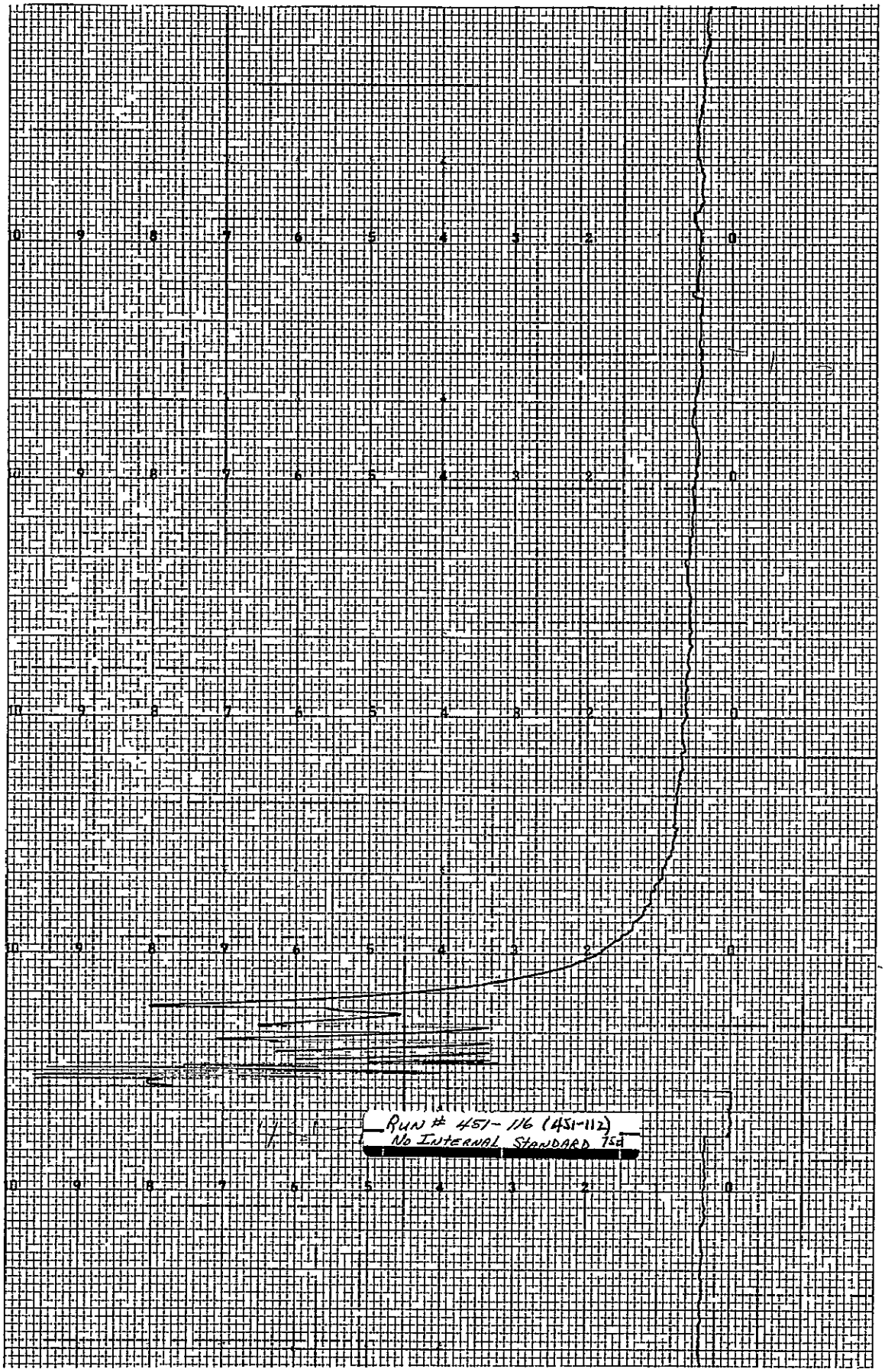
APPENDIX 61



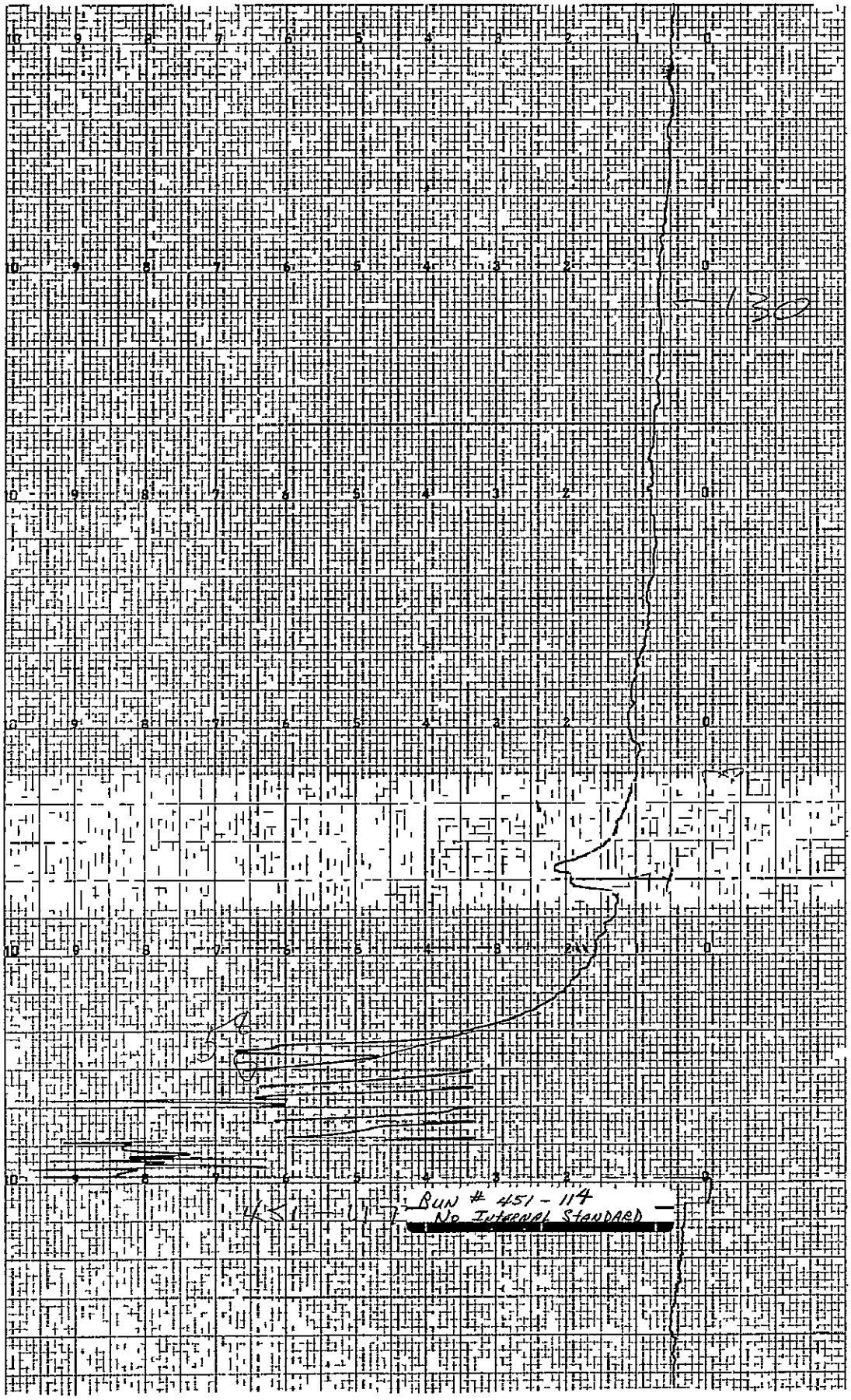
APPENDIX 62



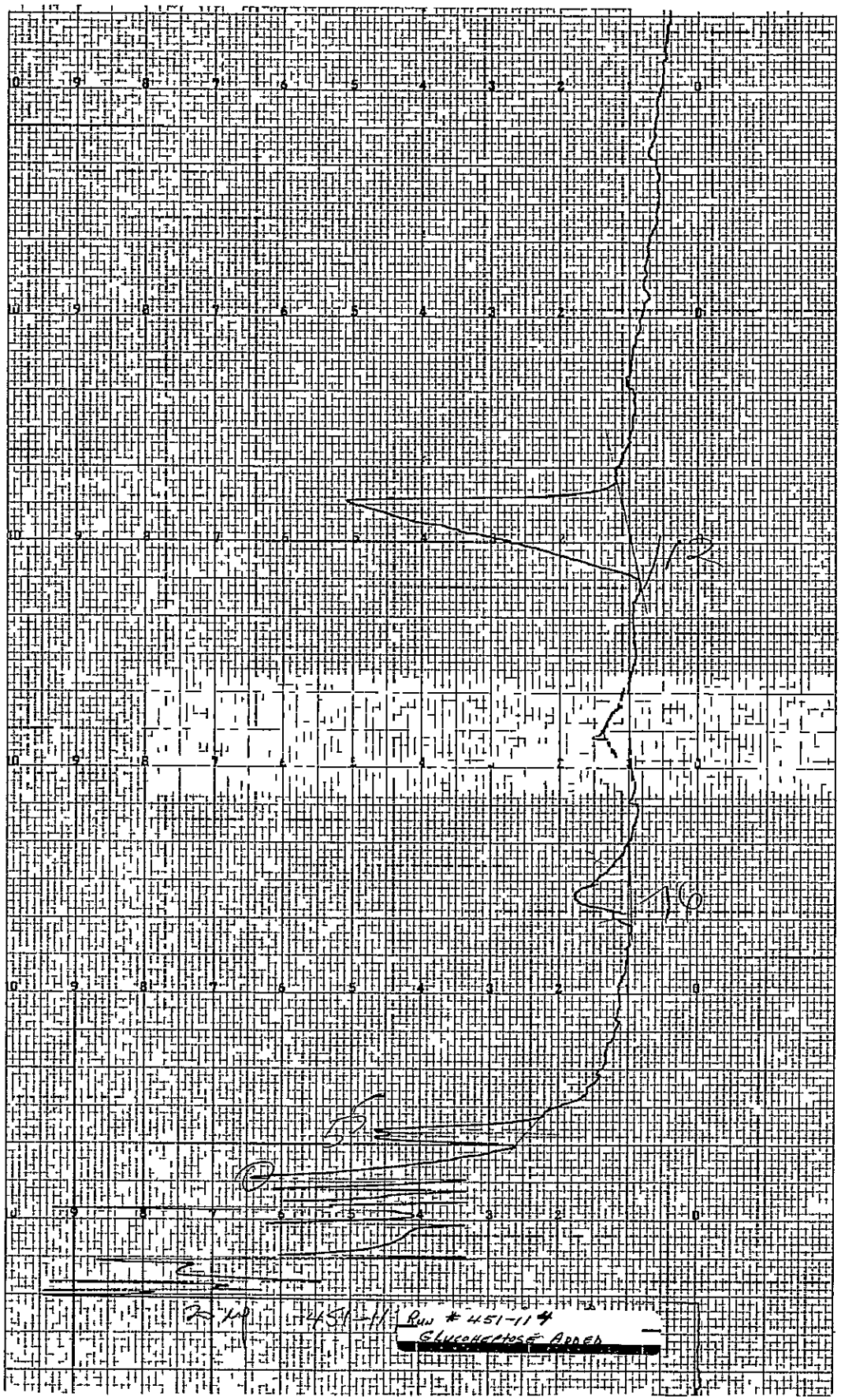
APPENDIX 63



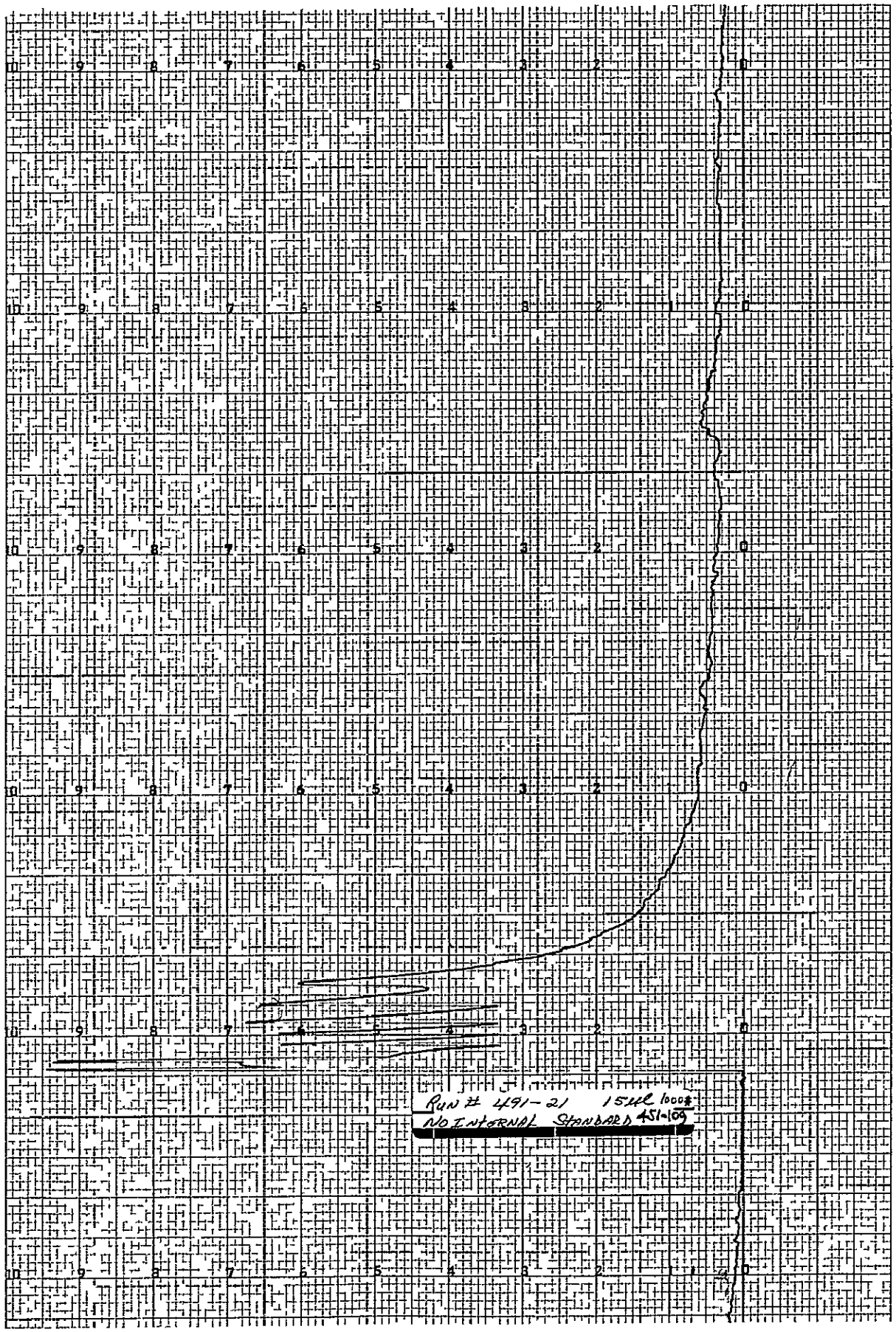
APPENDIX 64



APPENDIX 65



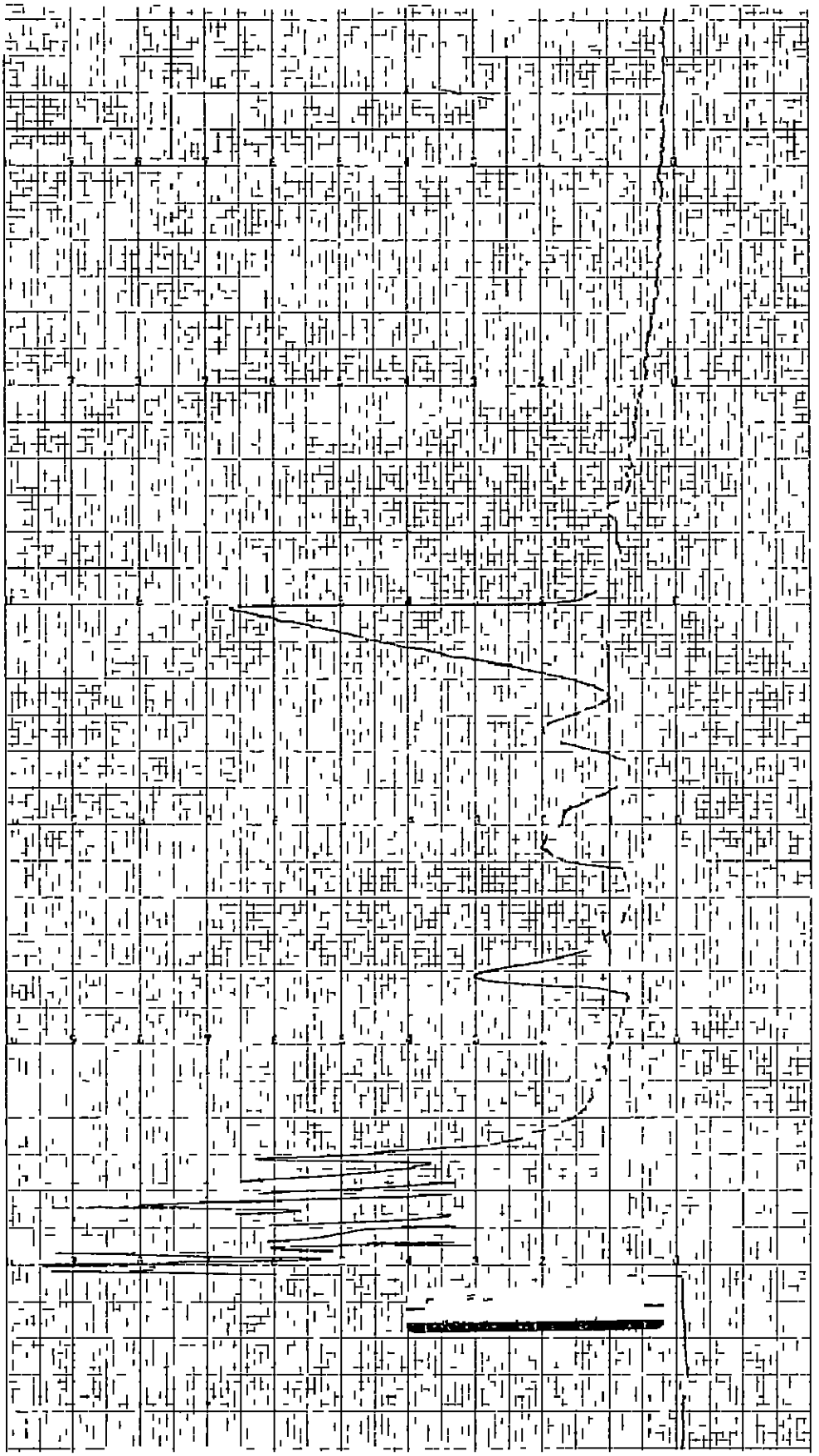
APPENDIX 66



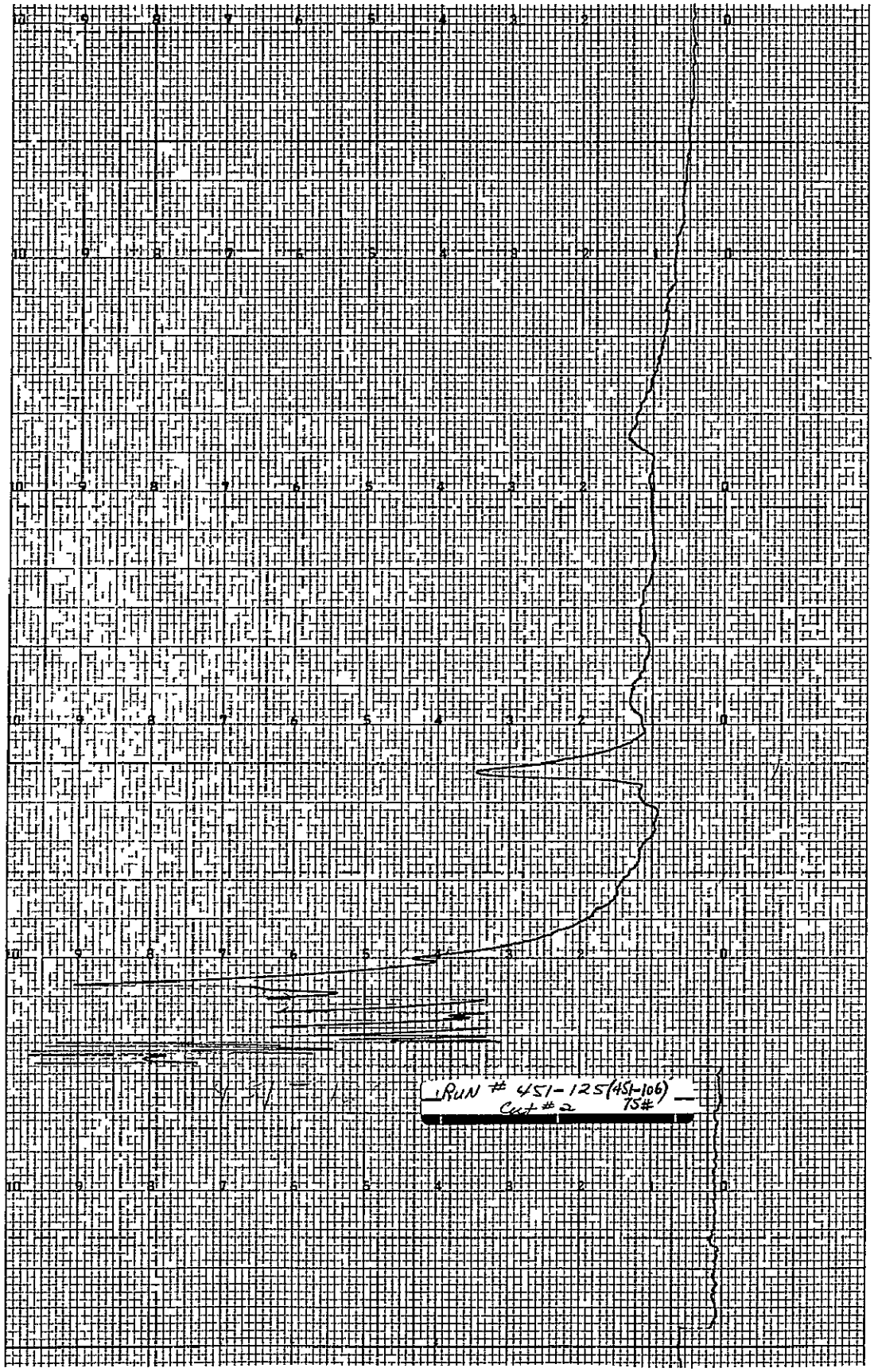
APPENDIX 67

APPENDIX 68

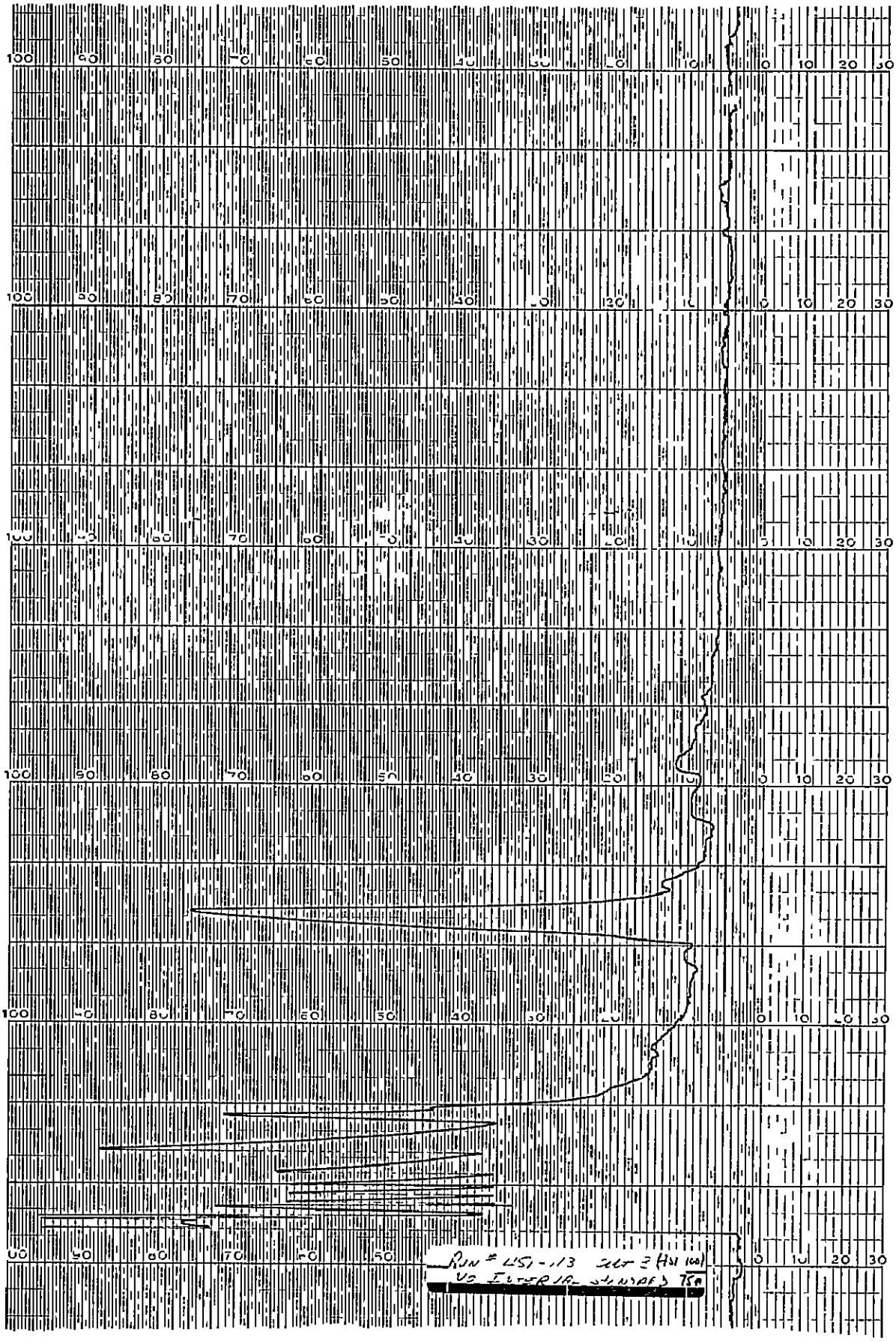
APPENDIX 69



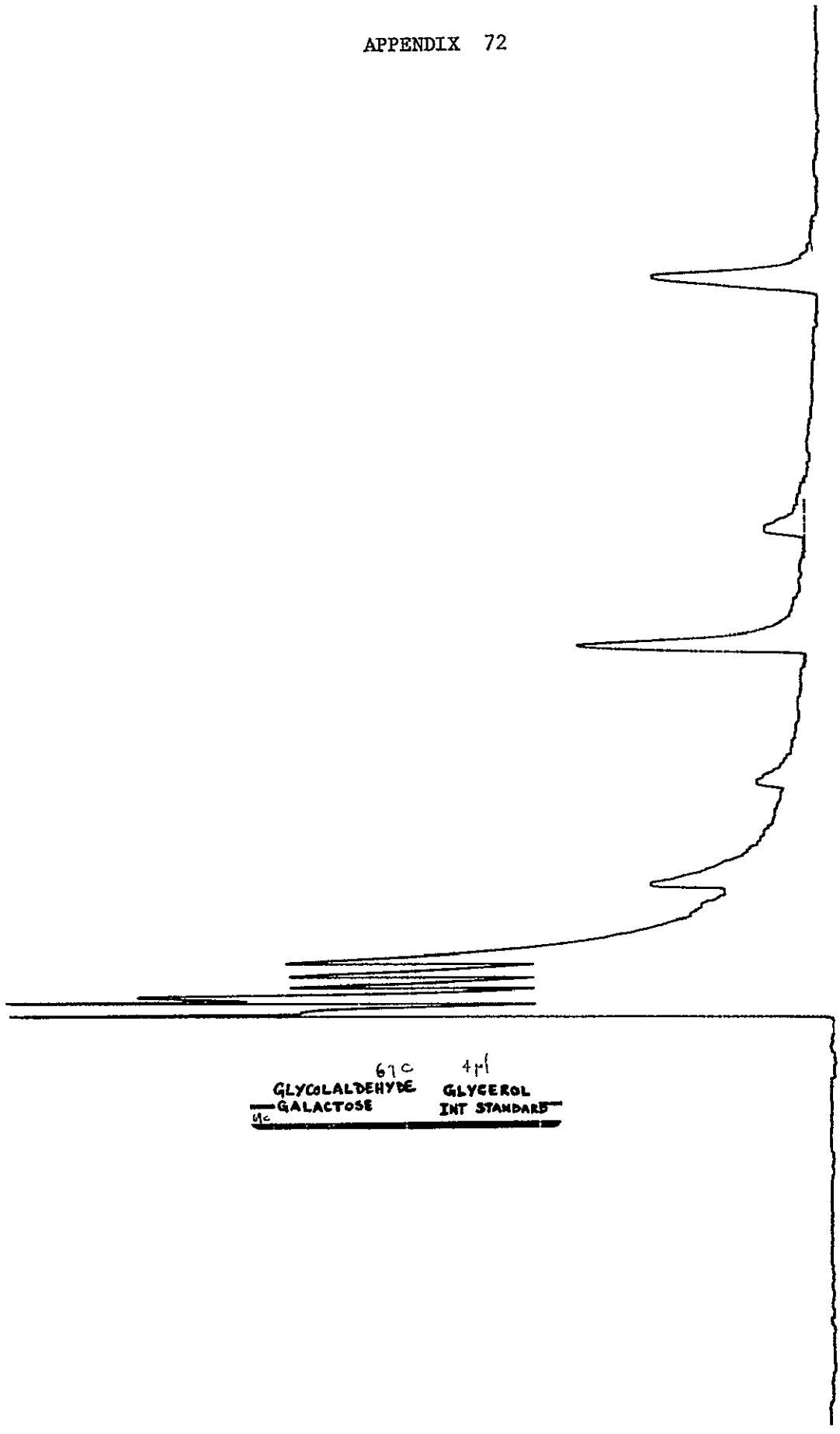
APPENDIX 70



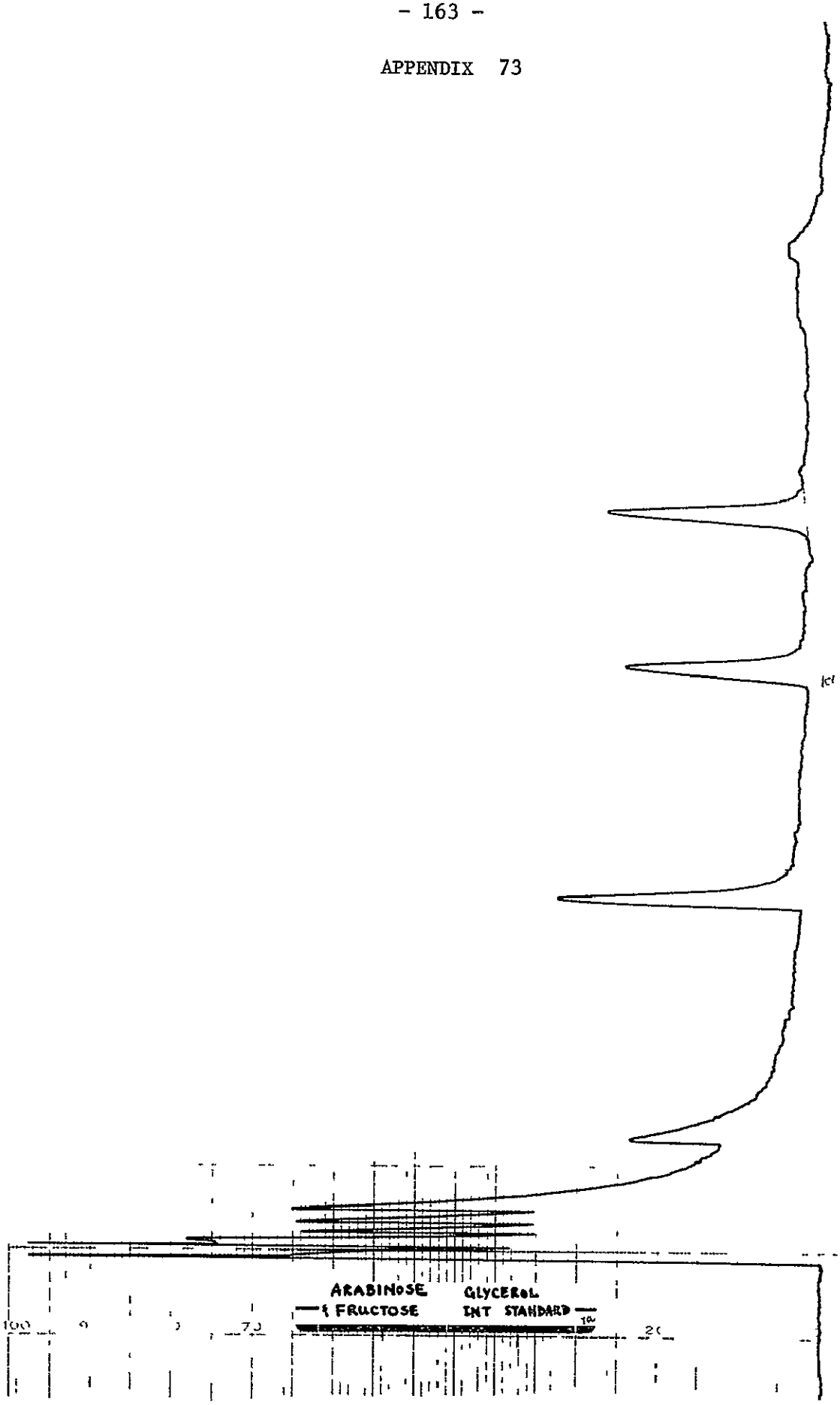
APPENDIX 71



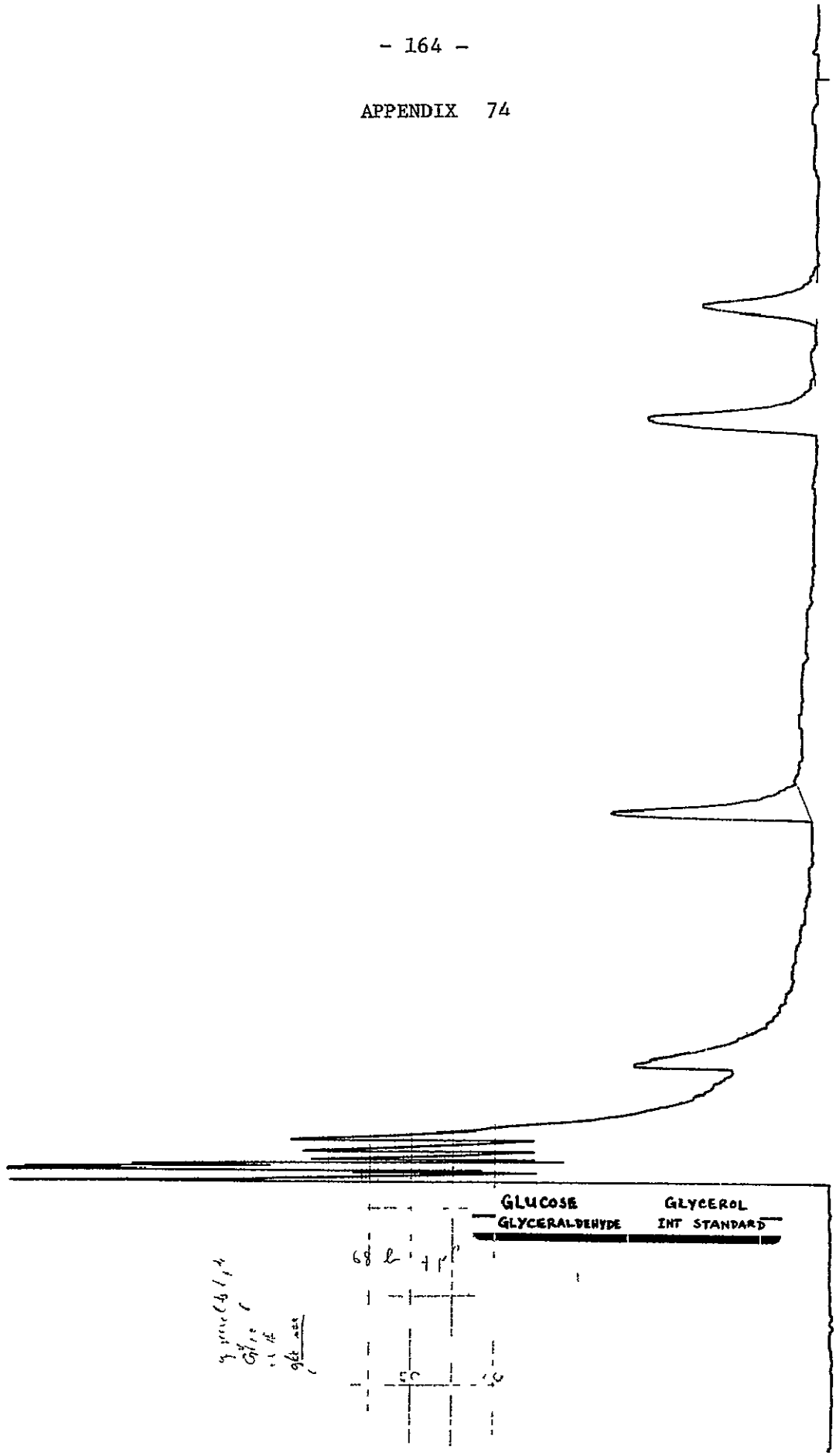
APPENDIX 72



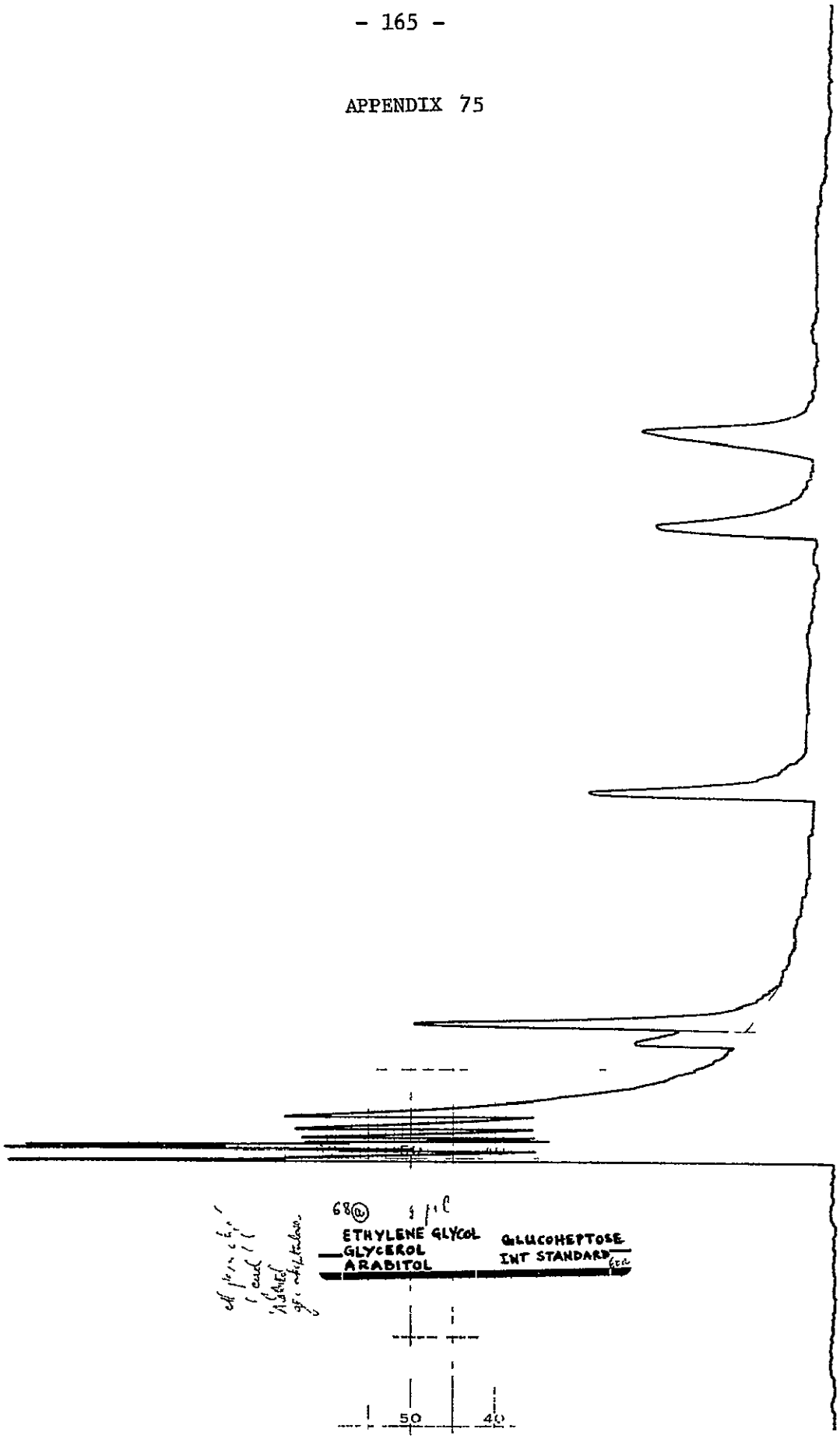
APPENDIX 73



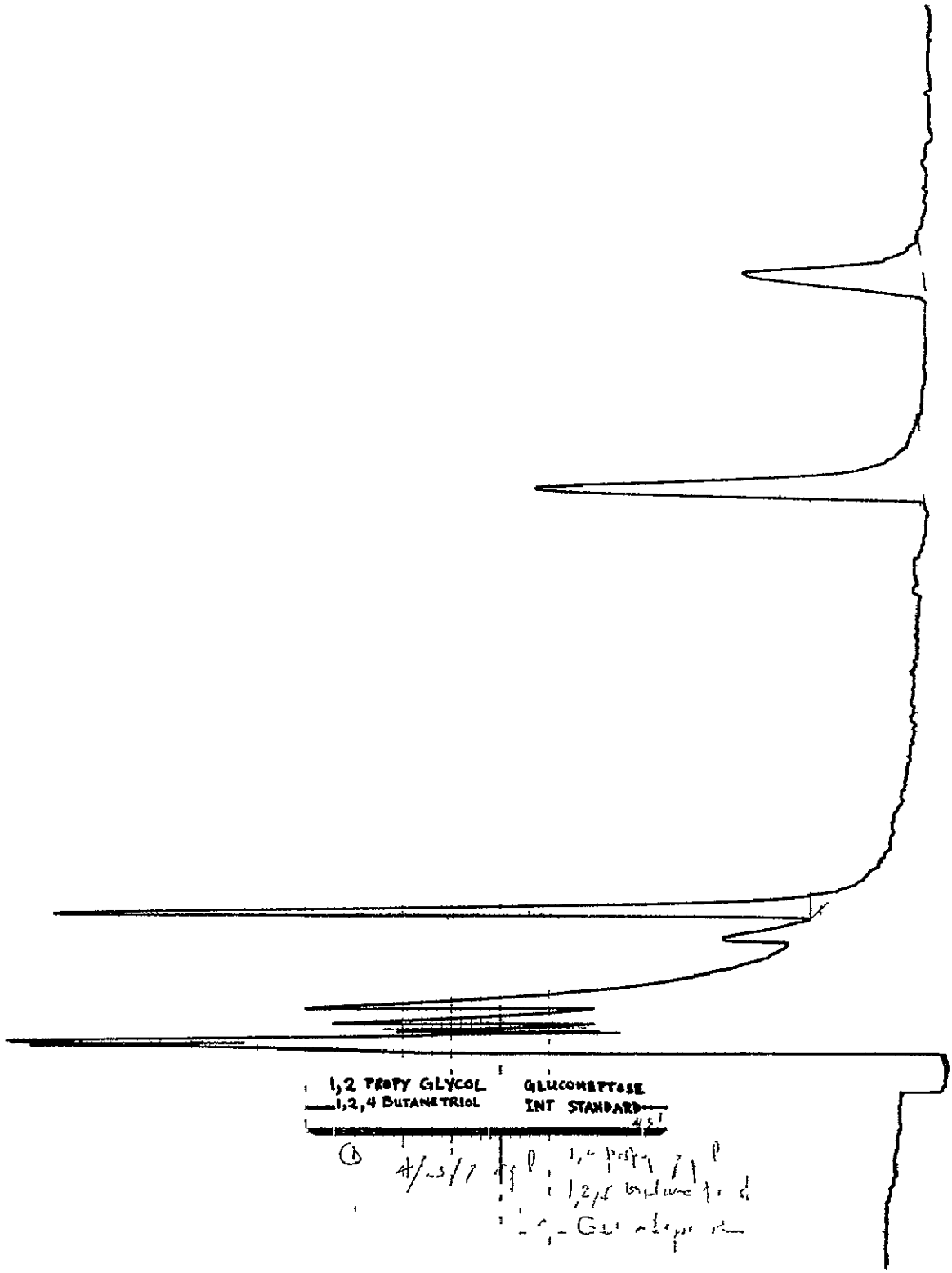
APPENDIX 74



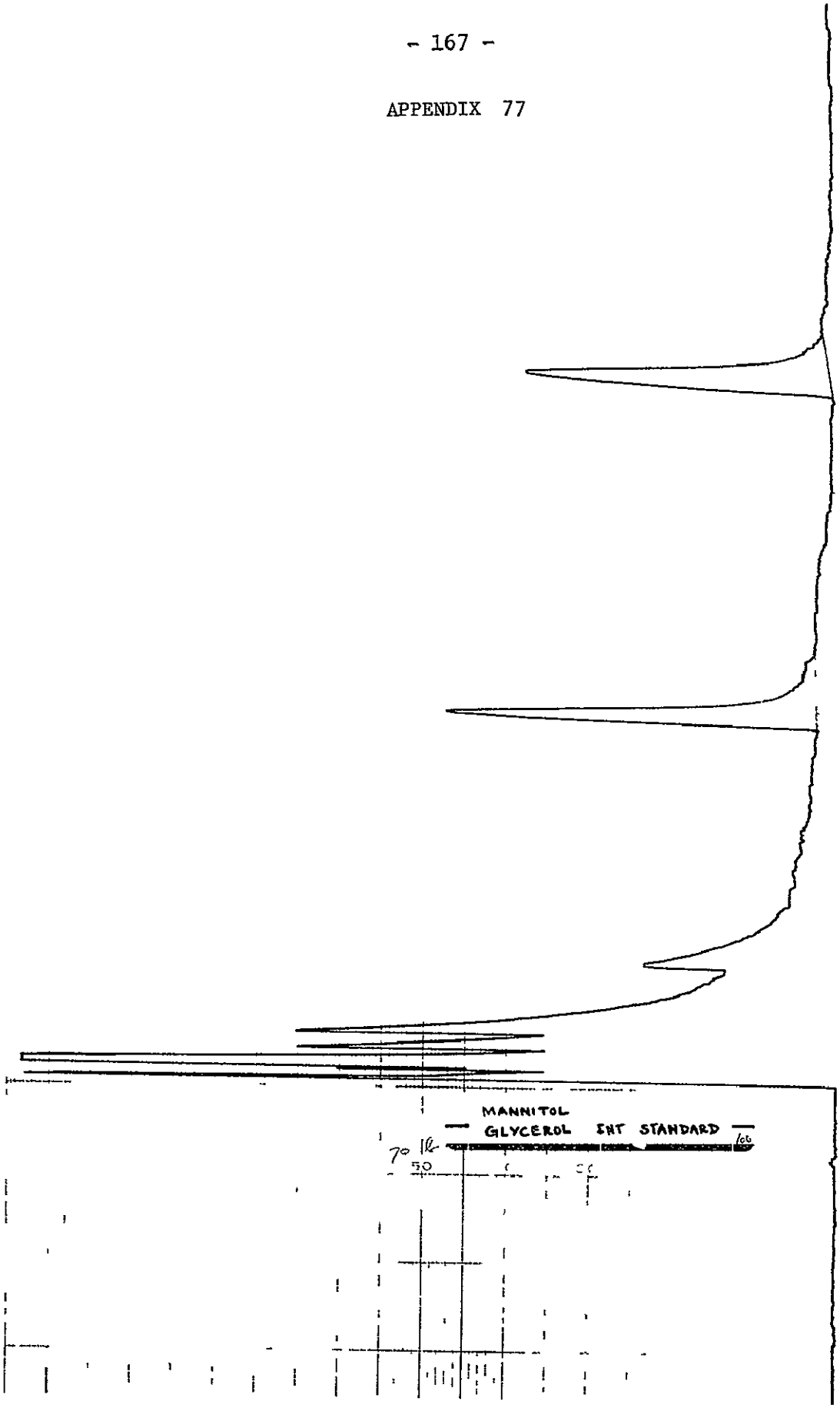
APPENDIX 75


ETHYLENE GLYCOL
GLYCEROL
ARABITOL
GLUCOHEPTOSE
INT STANDARD
50
40

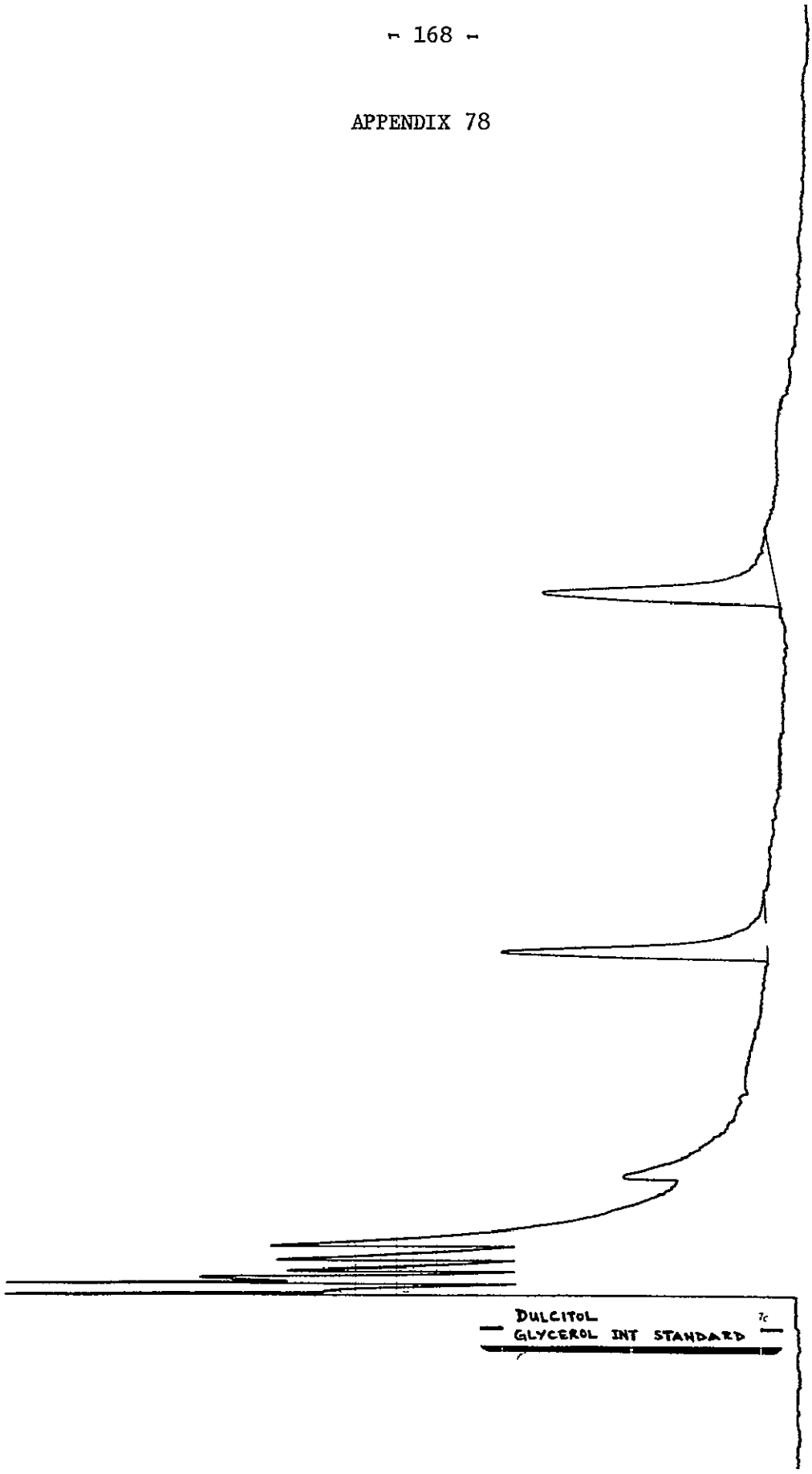
APPENDIX 76


1,2 PROPY GLYCOL
1,2,4 BUTANETRIOL
GLUCONEPTOSE
INT STANDARD

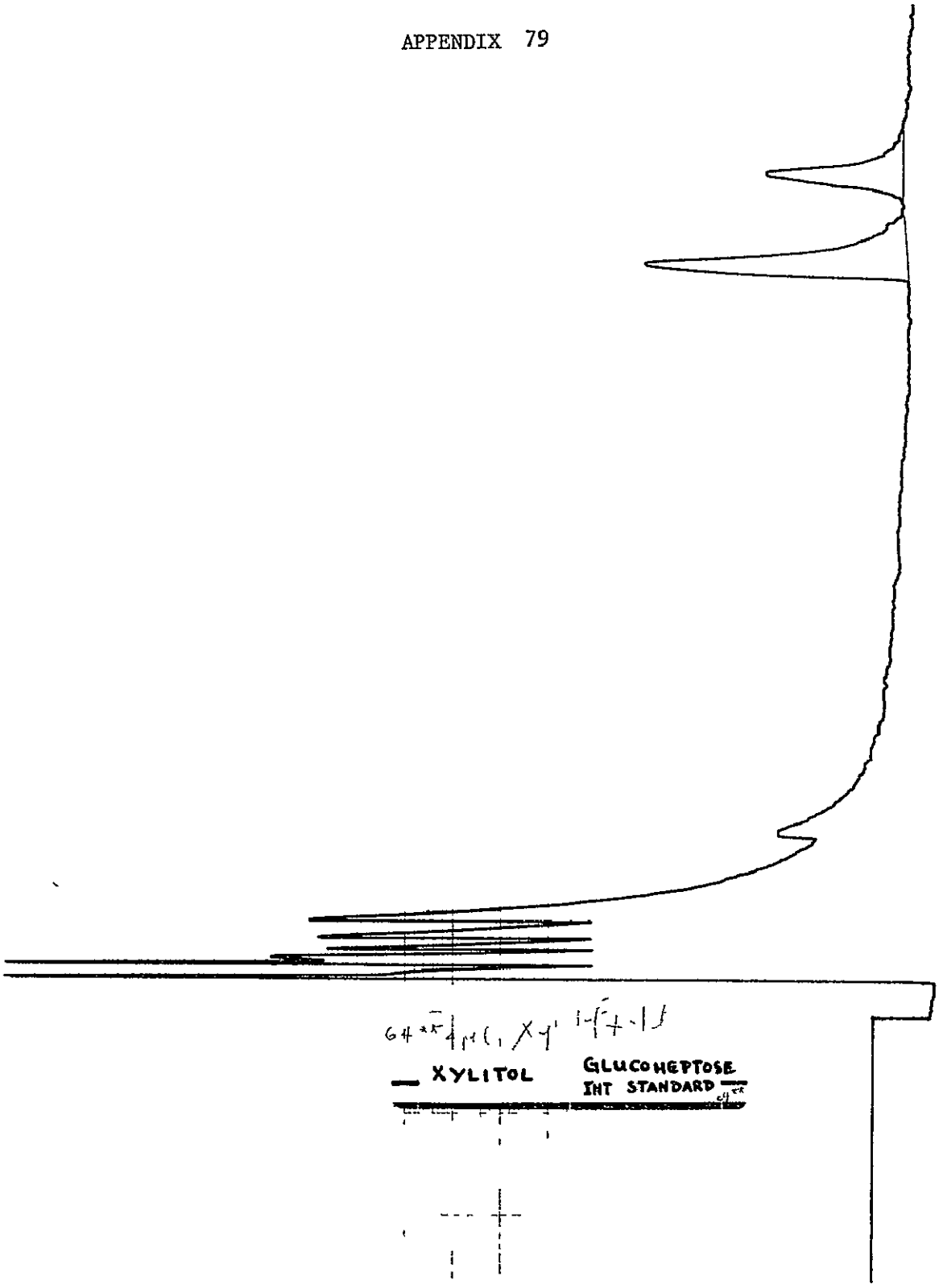
APPENDIX 77



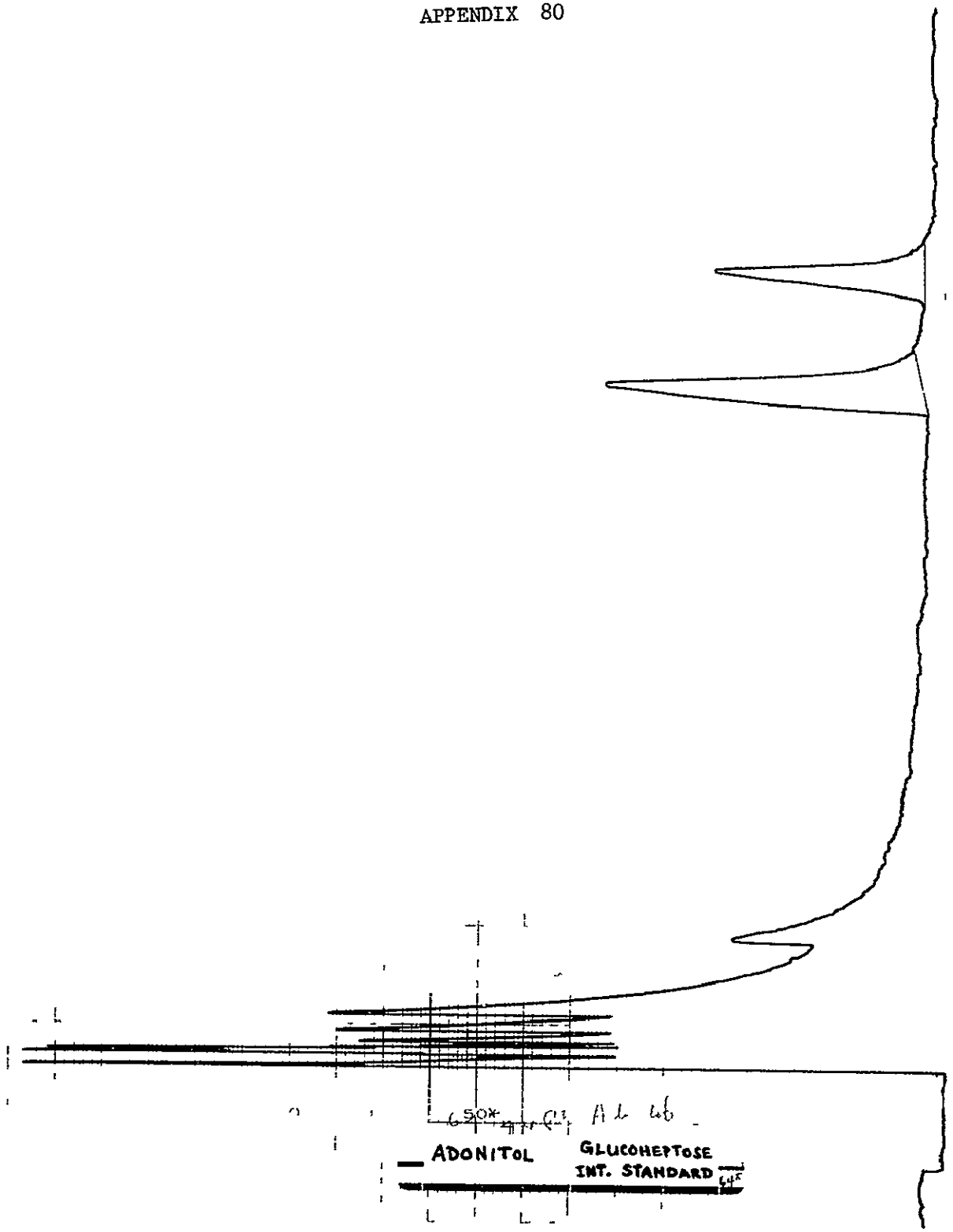
APPENDIX 78



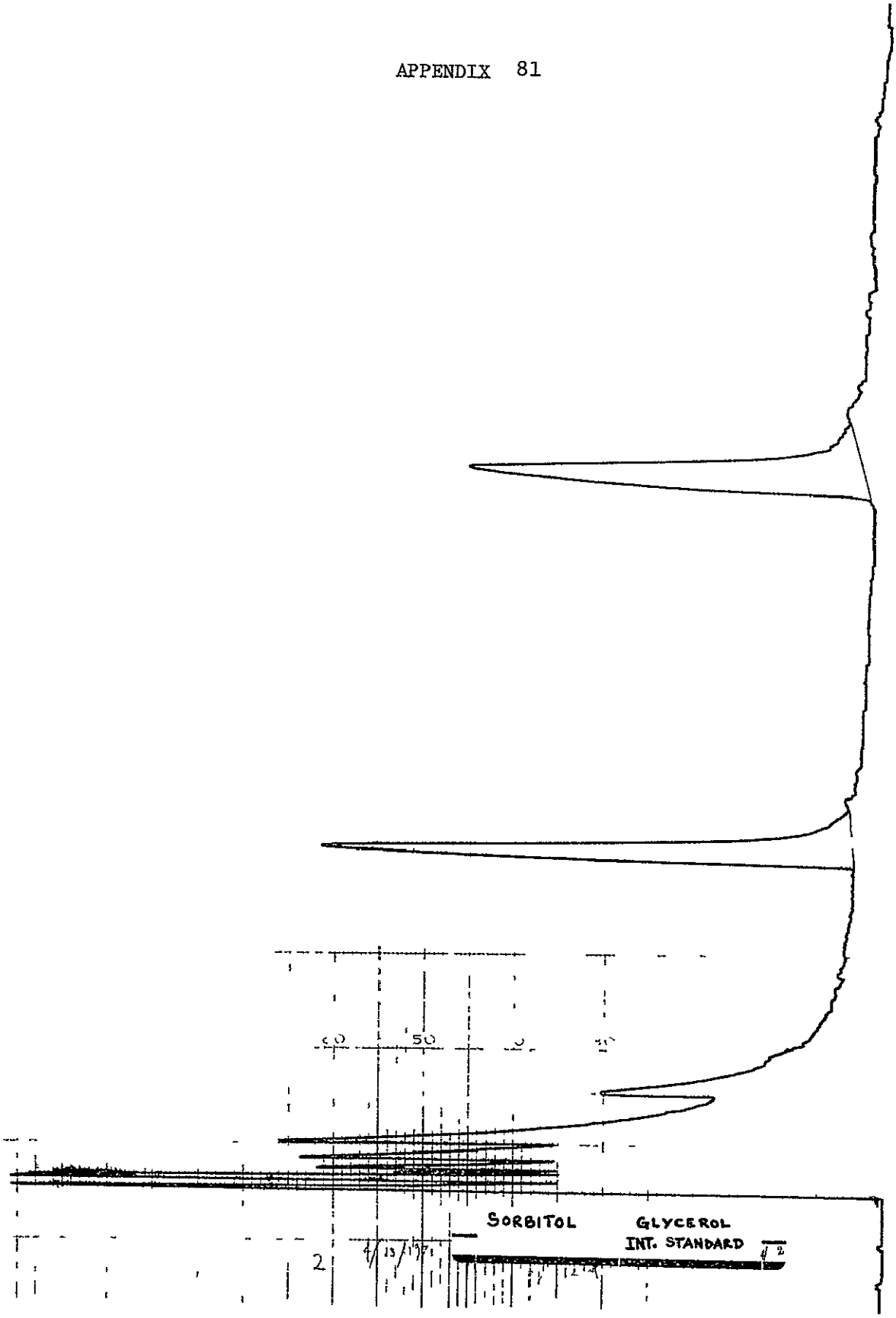
APPENDIX 79



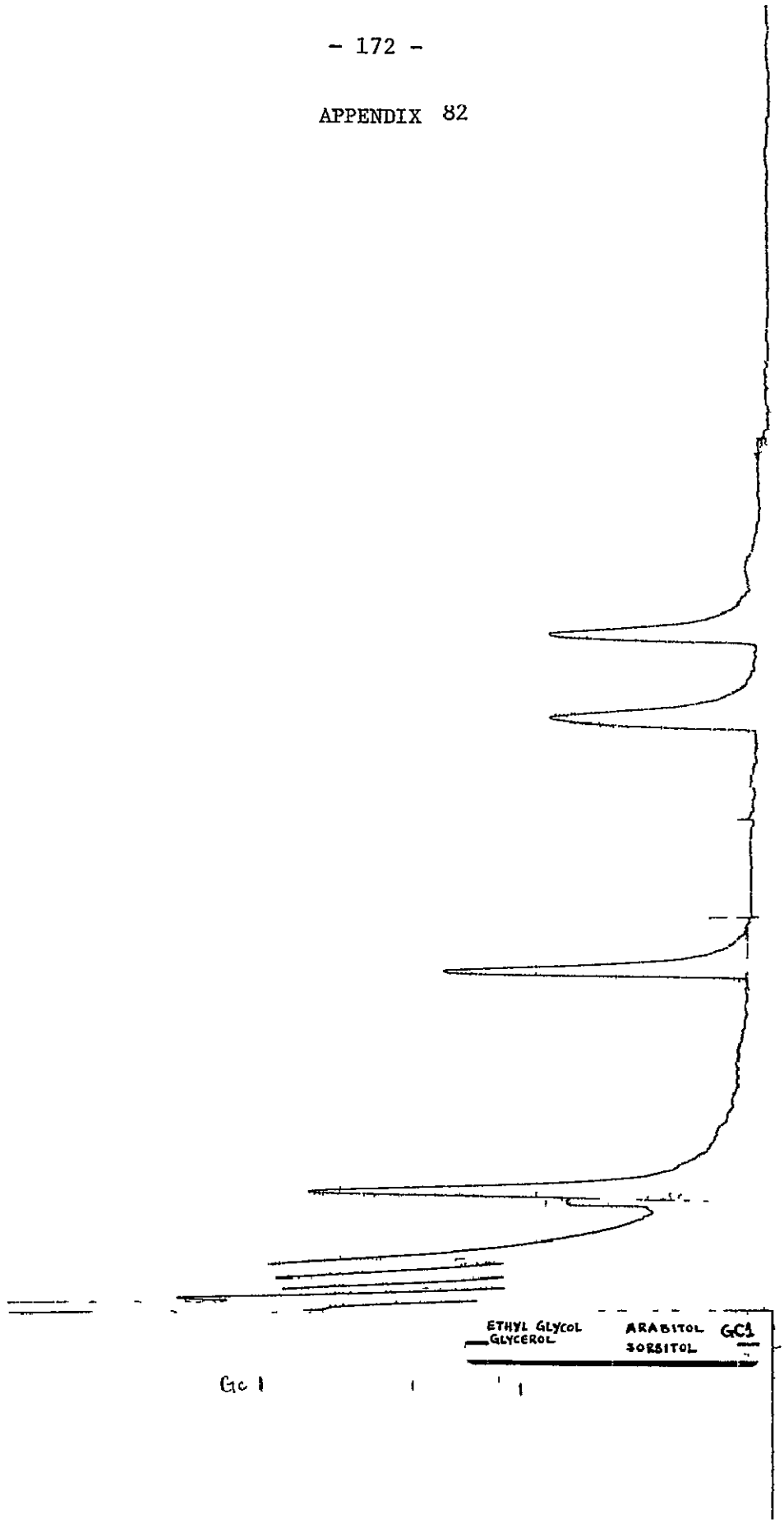
APPENDIX 80



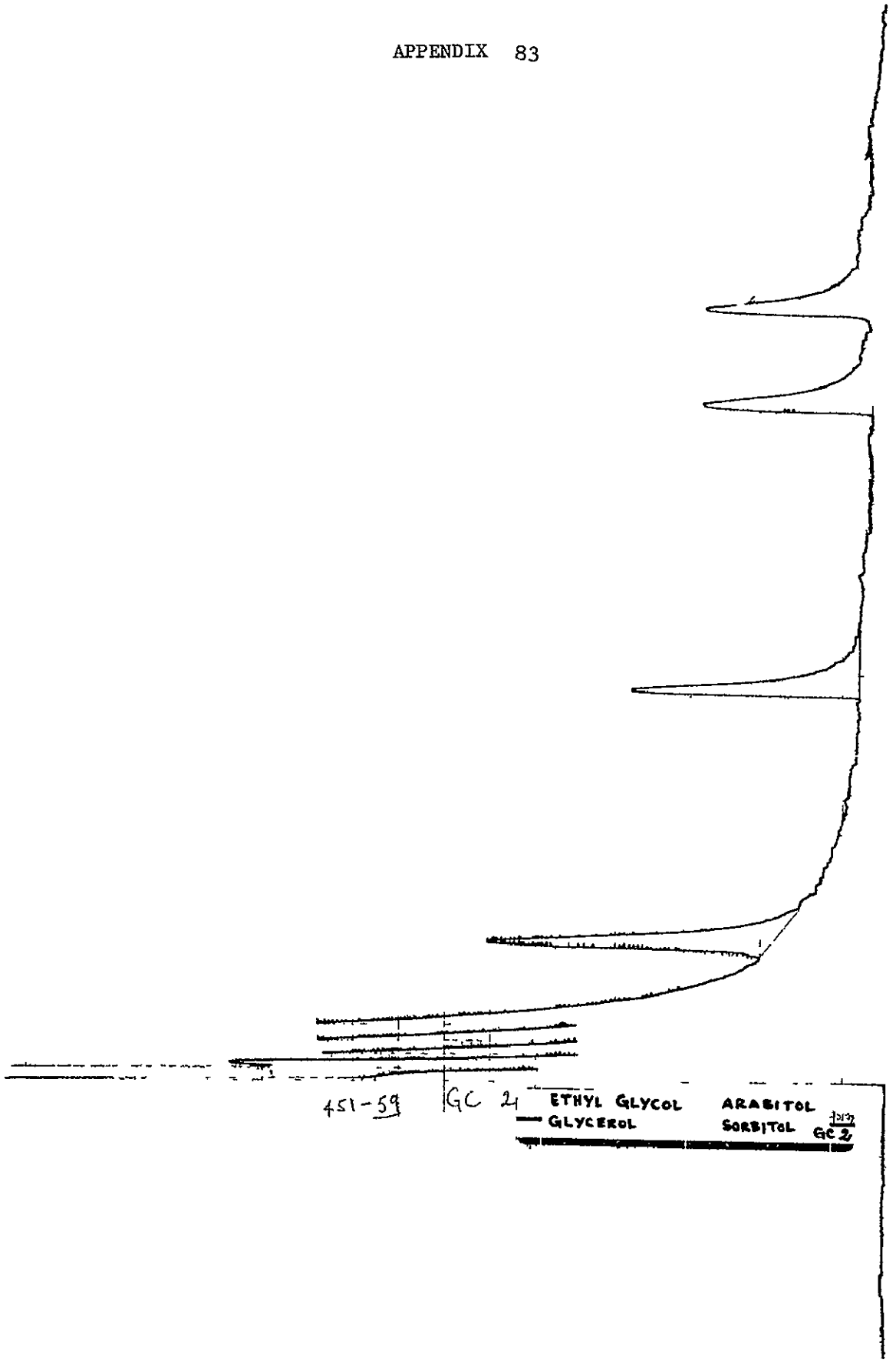
APPENDIX 81



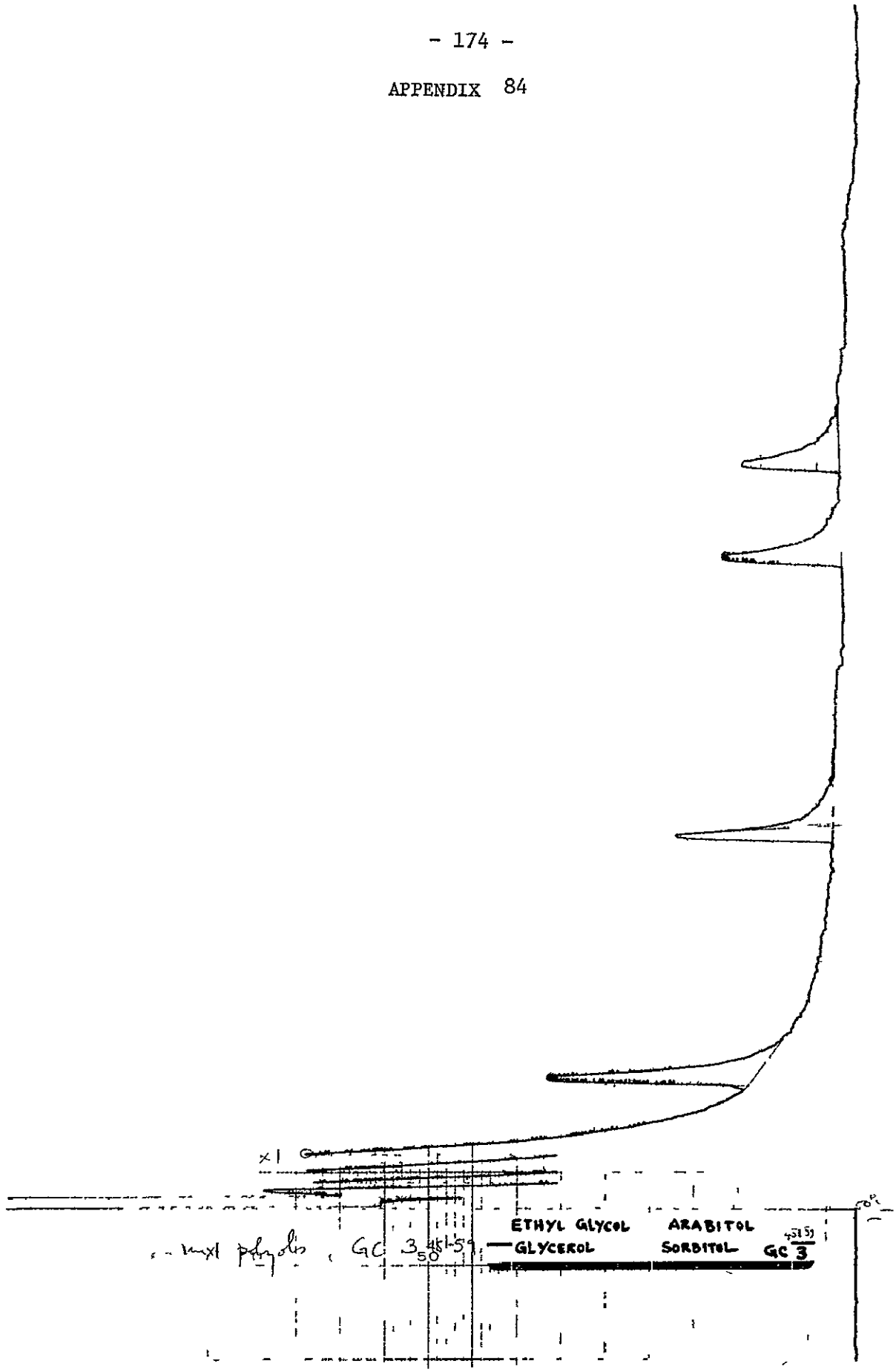
APPENDIX 82



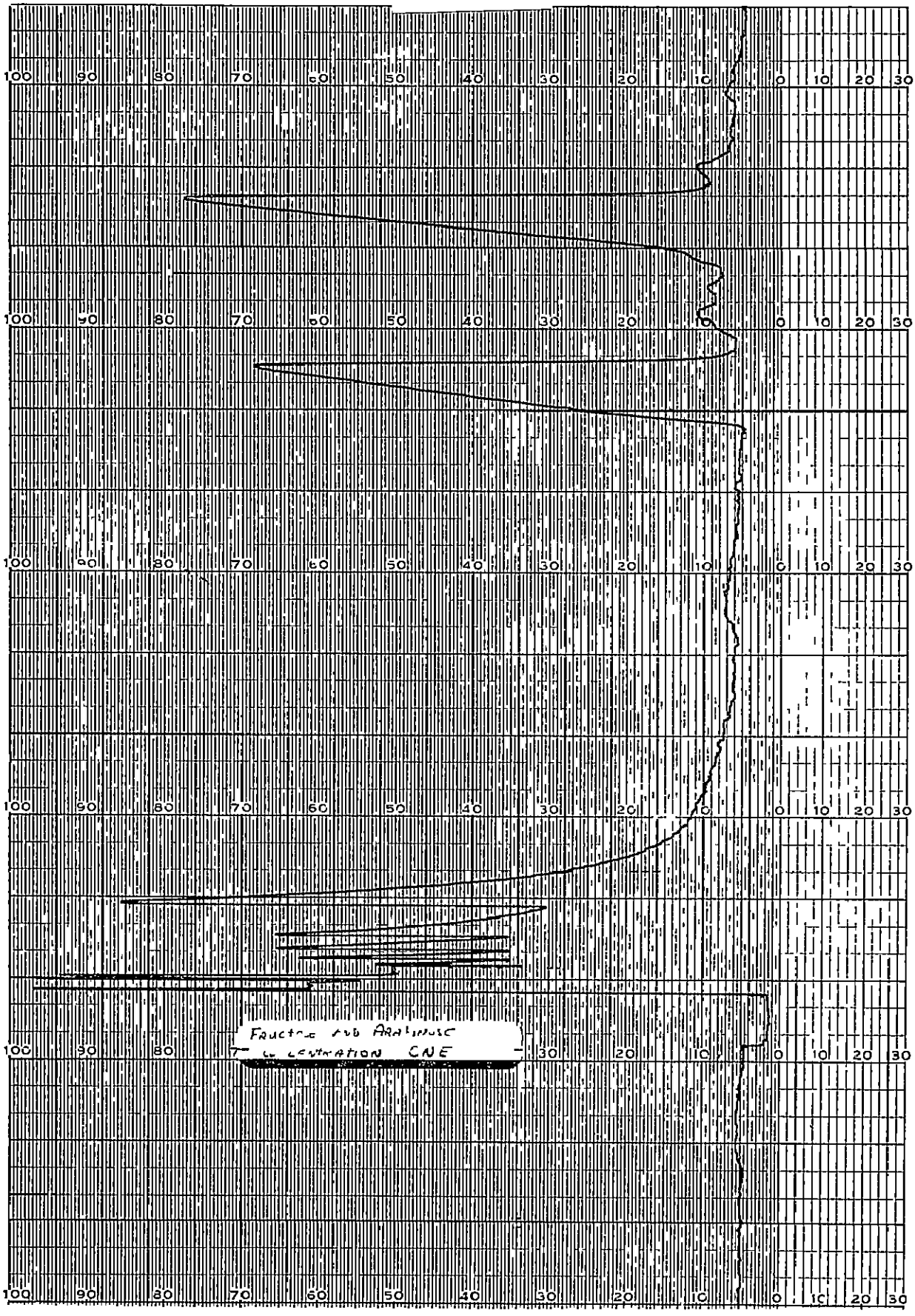
APPENDIX 83



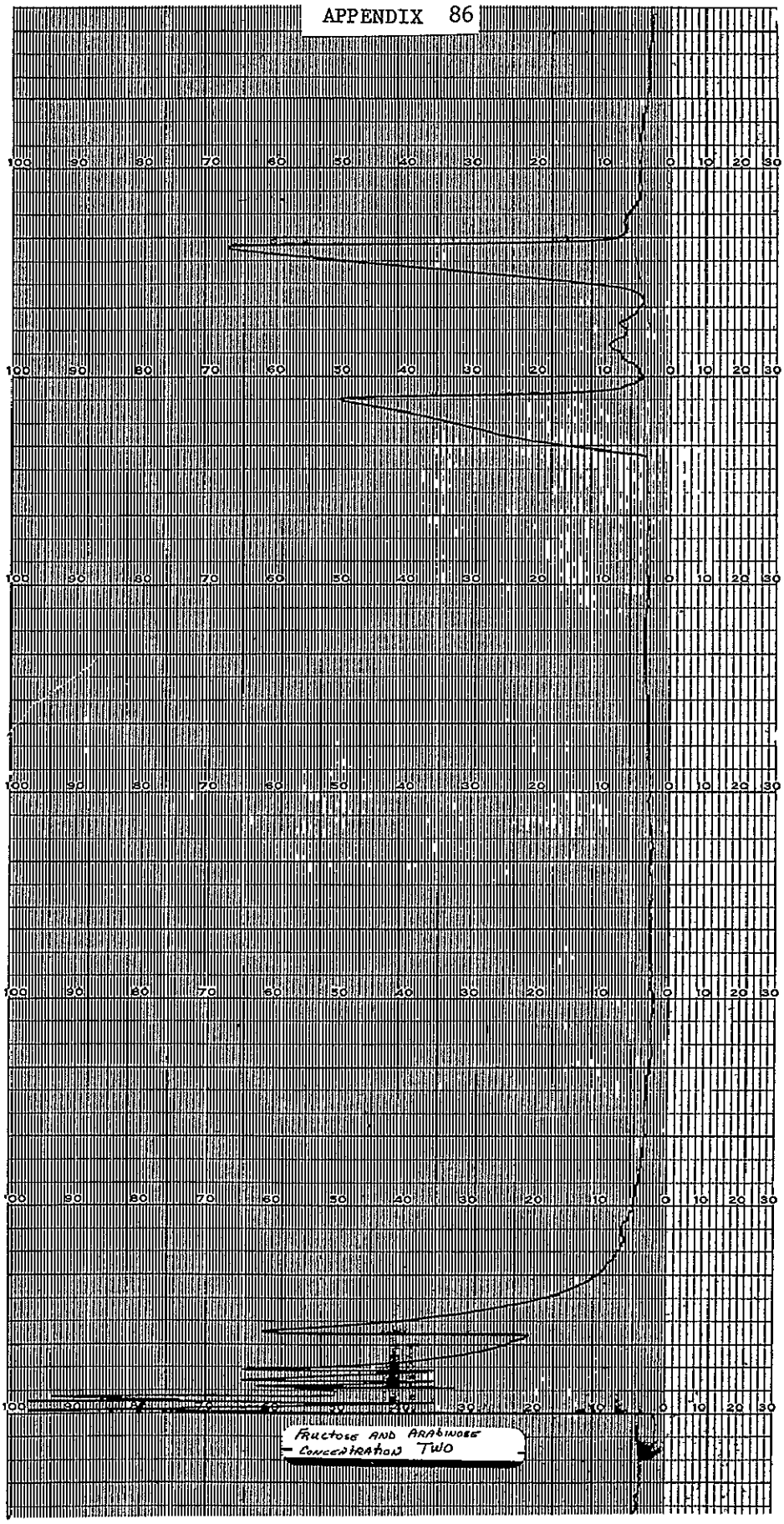
APPENDIX 84



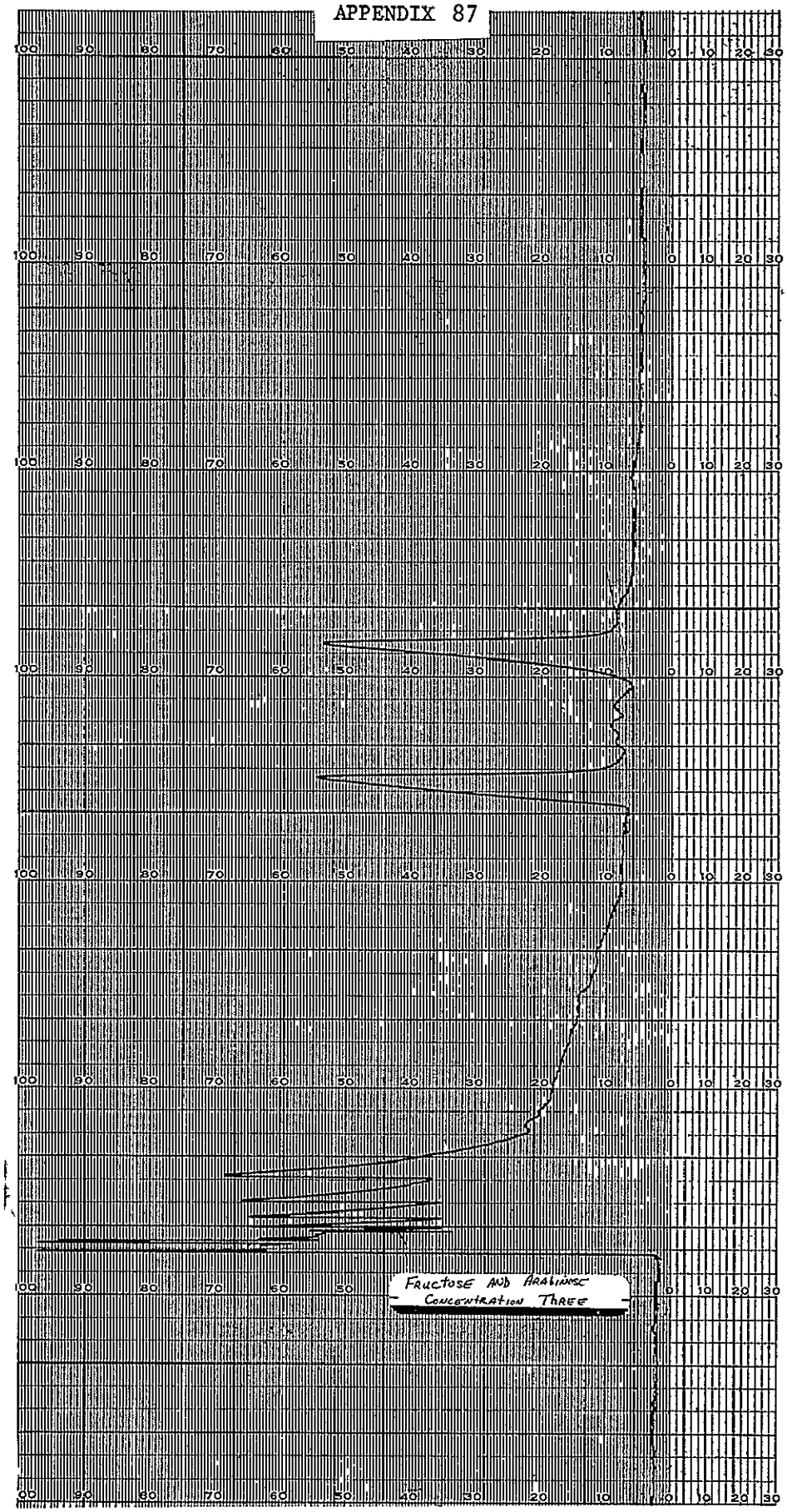
APPENDIX 85


100 90 80 70 60 50 40 30 20 10 0 10 20 30
Fructose and Arabinose
Concentration CNE

APPENDIX 86


100 90 80 70 60 50 40 30 20 10 0 10 20 30
FRUCTOSE AND ARABINOSE
CONCENTRATION TWO

APPENDIX 87



APPENDIX 88

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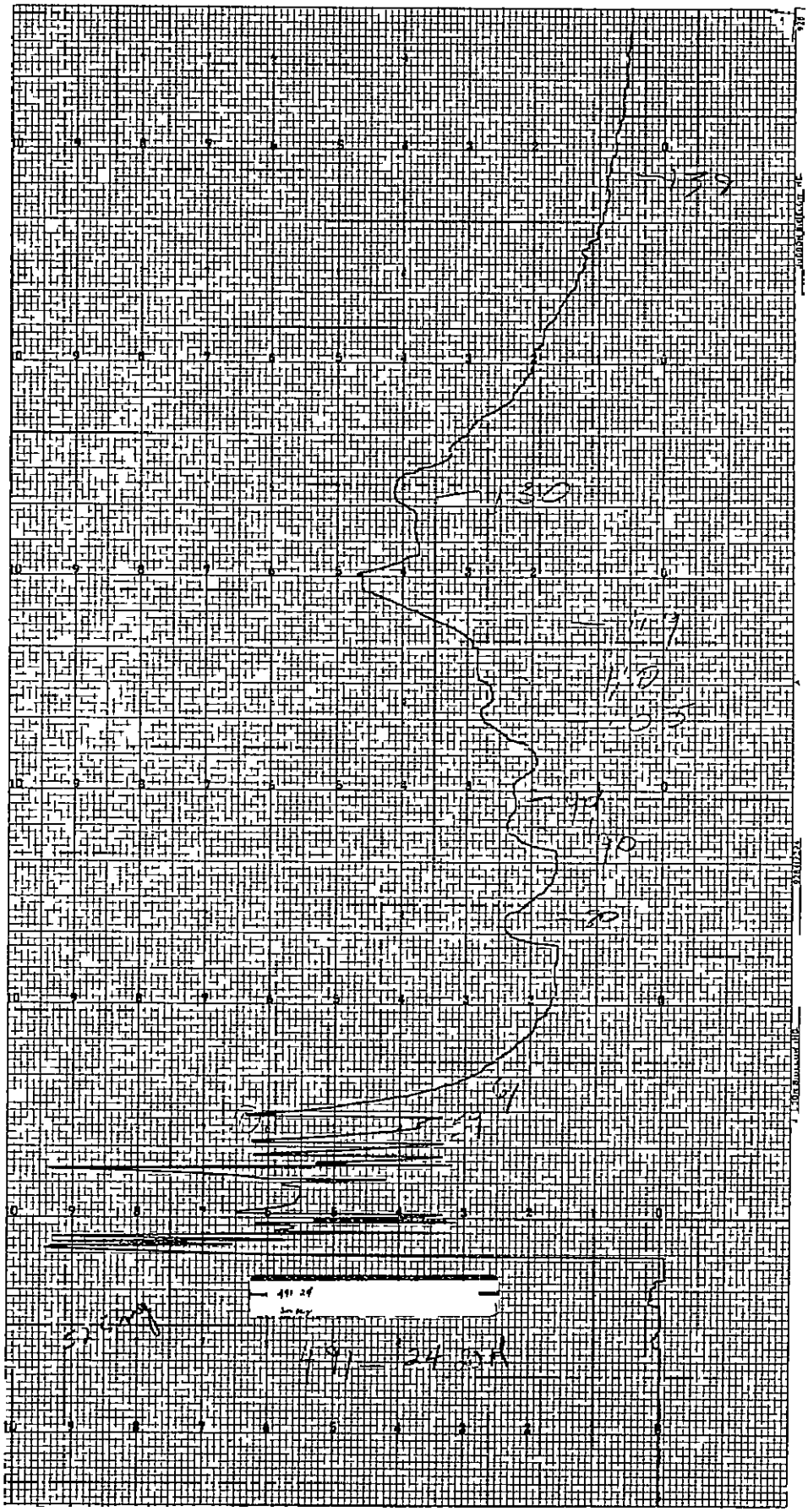

FIGURE 7

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Unclassified
Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY *(Corporate author)*

Esso Research & Engineering Company
Government Research Division
P. O. Box 8, Linden, N. J. 07036

2a REPORT SECURITY CLASSIFICATION: Unclassified

2b GROUP: None

3 REPORT TITLE

The Study of the Synthesis of Glycerol

4 DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Annual Progress Report 12 February 1970 - 15 November 1970

5 AUTHOR(S) *(First name middle initial last name)*

C M Kouidri
W F Taylor

6 REPORT DATE	7a TOTAL NO OF PAGES	7b NO OF REFS
November 1970		32

8a CONTRACT OR GRANT NO	9a ORIGINATOR S REPORT NUMBER(S)
NAS2-4496	
b PROJECT NO	
c	9b OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
d	

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11 SUPPLEMENTARY NOTES	12 SPONSORING MILITARY ACTIVITY
	National Aeronautics and Space Admin Ames Research Center

13 ABSTRACT

The approach to edible polyol synthesis which is based on driving the formaldehyde condensation reaction to the C_5-C_6 carbohydrate stage followed by reductive cleavage to glycerol and propylene glycerol was shown to be feasible, for the first time both edible polyols were produced directly from formaldehyde

Studies of the complex formose synthesis revealed that the reaction can be controlled to produce maximum yields of C_5-C_6 sugars The latter were found to be highest at the moment of complete or near complete entering formaldehyde conversion However, when reaction time exceeds that required for complete formaldehyde conversion other alkali-promoted reactions begin to occur and as a result, pentose and hexose content diminishes This was confirmed by studies in which formose mixtures generated under varying residence times were hydrogenolyzed under the best reductive cleavage reaction conditions The formose mixture which contained the larger quantity of pentose and hexose material yielded, upon hydrogenolysis, 22 08% C3 polyols. The poorer mixture, obtained under the longest residence time, afforded only 5 77% C_3 polyols

Conditions for the hydrogenolysis reaction of formose mixtures were obtained as a result of an extensive study of the catalytic reductive cleavage reaction of neat carbohydrates This study included investigation of the effects of catalyst type, carbohydrate structure, and hydrogen pressure on total C_3 polyol yield

Continued Page 182

ABSTRACT CONTINUED

The results showed that, while ruthenium on carbon used in conjunction with $Ca(OH)_2$ produced the largest quantities of edible polyols, it also promoted the hydrogenation of the pentose and hexose materials In fact, production of C_5-C_6 polyols was always larger than edible triol formation regardless of the nature of the starting material (i e , neat carbohydrate or formose mixture) Selectivity of the hydrogenolysis system to glycerol and propylene glycol must be improved in order to make the two-step process practical This can be achieved by designing and fabricating catalysts which will a) promote complete reduction of C_5-C_6 sugars to their corresponding polyols followed by cracking to glycerol or propylene glycol or b) cleave the starting material selectivity to C_3 fragments followed by hydrogenation to the desirable edible polyols

Separation via fractional distillation of glycerol from the hydrogenolysis product mixture was attempted. Glycerol was successfully separated from other components of the mixture Unfortunately, the presence in the still of materials which decomposed very near glycerol's distillation temperature prevented the collection of a pure sample. The problem of separating the edible propylene glycol from inedible ethylene glycol remains to be tackled

Unclassified
Security Classification - This Page

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Formaldehyde						
Synthetic Food						
Life Support						
Glycerol						
Propylene Glycol						