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The Thermal Decomposition of Sugar

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THE THERMAL DECOMPOSITION OF SUGAR

by

John Allen Williams

UC 1962

A thesis presented to the Department of Chemistry of
Union College in partial fulfillment of the requirements
for the degree of Bachelor of Science with a Major in
Chemistry.

By John Allen Williams

Approved by J. B. Porter

May 1962

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I would here like to acknowledge Prof. Robert Schaefer of the Union College Chemistry Department for his patient and understanding help in the instrumental analysis without which this work would not have been possible.

Gift of Author, January 10, 1963

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INTRODUCTION:

If one takes a cube of cane sugar and holds a lighted match or Bunsen burner to it, the sugar will not burn but will only melt and caramelize a little. If, however, a cube is touched to some cigarette ash and then held to a flame, the cube of sugar will burn with a sputtering blue flame and will continue to burn even after the flame is pulled away until all of the ash has dripped off the cube. This is the basis for a little-known after-dinner trick demonstrating the catalytic effect that some materials have on sugar.

OBJECT:

The primary object of the present series of experiments was to add information about the catalytic combustion of sugar to the present knowledge for the eventual determination of the reaction mechanism. The decomposition products of a simple sugar, glucose, with and without Na_2CO_3 catalyst were to be determined in an attempt to see what differences in the decomposition products, qualitatively or quantitatively, or in the decomposition temperatures were obtained. Vapor phase chromatography was tried as the means of analysis.

HISTORICAL:

One of the earliest references to the catalytic combustion of sugar with tobacco ash was made by C. Thomae in 1919 (9). Thomae assumed that the phenomenon was due to the presence of Fe_2O_3 in the ash.

In 1920 J. Arvid Hedevall published a report of experiments (4) in which he observed the effects of various additives on the combustion of cane sugar. He classified these

additives into three groups according to their effect on sugar combustion. These groups were:

1; Additives showing no change in observed combustion.

Included were BeO , Al_2O_3 , $\text{Al}(\text{OH})_3$, TiO_2 , SiO_2 , SnO , SnO_2 , As_2O_3 , Cr_2O_3 , MnO_3 , U_3O_8 , MnO , Fe_2O_3 (under certain conditions), NiO , Al and Ni filings.

2; Additives causing the sugar to burst into flames and emit smoke rings, yielding a normal ash.

Included were oxides of alkalis, alkaline earths, and heavy metals excepting those listed above.

3; Additives causing the sugar to burn with a flame and emit smoke rings, yielding a black porous residue.

Included were halogens and halogen salts (except CaF_2), P_2O_5 , H_2SO_4 , SO_2 , CuSO_4 , FeSO_4 , alkali and alkaline earth salts excepting $(\text{NH}_4)_2\text{CO}_3$.

Hedevall also observed that the intensity of the flame and the amount and shape of the residue were dependent on the additive.

In an article published in 1930, J. Fucherna (6) also discussed the effect of additives on sugar caramelization. Many specific examples were presented and were divided into three groups according to the coloration produced by, 1: dissolving the caramel and filtering, and 2; treatment with dilute NaOH . In addition he observed that the small coloration with alkaline reactions formed by acetates and chlorides indicates a decomposition of sucrose into glucose and fructose with non-alkaline reactions which readily gives rise to

coloration.

Fucherna also stated that sucrose liberates an equivalent quantity of an acid when the salt of that acid is used as the additive. Additives of one of the groups when added in sufficient quantity, caused foaming and intensive odors suggesting C_6H_5CHO . These solutions became acid. Also proposed was that sucrose may exert its dielectric properties as a solvent for the salts capable of dissociation. The abstract is mainly a jumble of observations, seemingly unrelated, some of which appear to be contradictory.

In 1935 E. H. Riesenfeld and F. Muller published an article (8) in which they stated that the alkali salts in the tobacco's ash had more effect on the combustion of sugar than the iron content as originally proposed by Thomas.

In the same year J. A. Ambler and S. Byall published the results of experiments dealing with "Impurities in White Sugar" (1). They also divided the nonsugar additives into three classes according to their effect on sucrose. These classes were:

1; Additives that increased inversion of sucrose and decreased caramelization. The resultant hot syrups were acidic.

Included were salts whose aqueous solutions are neutral or acidic.

2; Additives that decreased inversion of sucrose and increased caramelization. The resultant hot syrups were alkaline.

Included were salts which react as alkaline and salts of strong bases with volatile acids.

3; Additives that increased inversion of sucrose and increased caramelization due to secondary reactions of non-sugars with the invert sugar.

Included were NH_4^+ salts, amino acids, and iron salts.

As with Pucherna, Ambler and Byall found that the acidic properties of sucrose increased with increasing temperature. This amounts to an auto-inversion of the sucrose by heat. In reference to the above groupings they observed that ions of strong acids were formed in hot solution for neutral salts of group 1. These did not volatilize until a high temperature was reached. For the additives of group 2, they stated that the resultant alkalinity acts as a buffering agent and inhibits the inversion. The non-sugars of group 3 were observed to be acidic in solution. It was also proposed that the reaction involved in alkaline solution is a decomposition of sucrose with formation of reducing substances of aldehyde or ketone types with small inversion due to localized momentary liberation of H^+ . Caramelization was thought to be due to a further decomposition by heat of the invert sugar formed and reducing substances containing carbonyl groups.

J. E. Day, in 1936 (2) listed a large number of metal oxide catalysts in order of their effectiveness on the oxidation of carbon. A large number of heavy metal oxides were significantly on the positive side.

In 1961, R. M. Day (3) observed that the presence of additives which catalyzed the combustion of sugar caused a significant decrease in both the melting point and the

decomposition temperature of sucrose. By similar observations on mannitol it was concluded that the catalysis was generally independent of the carbonyl groups and ether linkages in carbohydrates. It was also shown that Na_2CO_3 , halides of heavy metals, and NH_4Cl had a moderate to strong effect on catalysis; NaCl and heavy metal oxides had no or little effect. The rate of decomposition of sucrose with Na_2CO_3 and HgCl_2 were determined by thermogravimetry with relatively inconclusive results.

Most of the literature up to the present time dealing with combustion and related effects of sugar concerns itself mainly with experimental observations. No mechanism seems to have been put forth. This is most likely due to the probable complexity of the mechanism or to the possibility of more than one.

APPARATUS:

Gas Line: In attempting to determine the decomposition products a gas line was first set up. The arrangement of the units are shown in the accompanying diagram #1. Nitrogen was passed over the sample sugar being decomposed to provide an inert atmosphere and prevent oxidation. The nitrogen then acted as a carrier for the decomposition products delivering them to the individual traps further on in the line.

Two Dewar flasks containing dry ice - acetone mixtures were used as cold traps. A side arm test tube containing a long piece of glass tubing was placed into the top of the

Dewar. The tubing acted as inlet and the side-arm as outlet for the nitrogen line. The first cold trap was used to collect any moisture or hydrocarbon impurities present in the nitrogen before it entered the gas line. The second was used to trap the H_2O , CO_2 , and volatile hydrocarbons given off by the decomposing sugar. These were to be analyzed later by vapor phase chromatography.

The decomposing flask was immersed in a paraffin bath for temperature regulation. A thermometer was placed in the paraffin. The nitrogen line was passed through the bath in a spiral of brass tubing before entering the flask. This was an attempt to minimize any cooling of the sample at high temperatures due to the incoming gas. The bath was heated with a Bunsen burner. Because of the danger of inflammability and the quantities of smoke given off at high temperatures, the paraffin was replaced by a silicone bath composed of silicone oil plus 0.06% by weight of iron in iron octoate to prevent decomposition of the silicone oil at high temperatures. An electric heating element also replaced the Bunsen burner. This was made by placing a coiled nichrome wire in a coil of Pyrex glass tubing and placing this in the bath underneath the flask. The temperature was controlled by varying the voltage with a Variac variable voltage control. The temperature bath was stirred by hand.

The long horizontal Pyrex oxidation tube was partially filled with CuO granules and heated with a Bunsen burner during the runs. Any CO and H_2 carried from the decomposi-

tion flask were oxidized to CO_2 and H_2O here and collected further on in the line.

Two bubble traps half filled with KOH solution were used to collect CO_2 by producing K_2CO_3 . These tubes were to be titrated after each run to determine the amount of CO_2 gain. The first trap collected any CO_2 not taken out of the line by the cold trap. The second trap collected CO_2 which was formed from the oxidation of any CO present in the decomposition products. The oxidation was carried out in the oxidation tube.

Two CaCl_2 drying tubes were used in the line. The first, a U-tube, was used to dry out the nitrogen carrier after passing through the first bubble trap. The second consisted of a Midvale bulb which was weighed before and after each run to determine the amount of water produced from the oxidation of any H_2 present in the decomposition products.

This gas line had several serious drawbacks. A significant pressure built up in the line due to the bubbling through solutions. Leakages readily occurred even when rubber stoppers replaced corks. One cold trap following the decomposition flask was not sufficient and much of the products dissolved in the succeeding bubble trap. In addition, the cold trap clogged up after about 30 minutes of run preventing any continuation of the experiment. The entire set up was cumbersome and the analysis was time consuming.

Intermittent Gas Sampling: Because of the many drawbacks to the gas line and to increase the ease and speed of deter-

mining the decomposition products the individual absorbing tubes and traps were done away with. The apparatus arrangement is shown in diagram #2. The decomposition products were sampled intermittently by the vapor phase chromatograph directly from the decomposition flask at various temperatures as the sample temperature was being raised. In order to prevent condensed products flowing into the gas sampler, the delivery tube was coiled. A bubble counter was placed at the outlet of the gas sampler to permit determination of the relative flow rate of the nitrogen. Almost all of the experiments were carried out using this type of sampling technique rather than the cold traps.

Distillation: To obtain a liquid sample of the decomposition products a distillation arrangement was set up as shown in drawing #3. The silicone oil bath arrangement was again used for temperature regulation. Nitrogen gas was slowly passed through the decomposition flask as in the intermittent gas sampling technique in order to avoid oxidation. It then carried the vapors of the decomposition products through a condenser and finally into a flask cooled in an ice bath where the distillate was collected.

Infrared Spectrometry: The attempt at identification of distillates and residues with acetic acid was carried out on a Perkin-Elmer Model 21 Infrared Spectrophotometer.

Vapor Phase Chromatography (VPC): A Perkin-Elmer Model 154 Vapor Fractometer with an attached automatic Leeds and Northrup Speedomax Vapor Fractometer Recorder was used

for the major portion of analysis carried out in these experiments. For liquid samplings 10 μ l was introduced into the chromatograph with a microliter syringe. For gaseous samples, a 0.25cc gas sampling valve was first used to sample directly from the decomposition flask. When it later became evident that this did not provide great enough sensitivity it was replaced by a 5.0cc gas sampling valve.

Two fractometer columns were used. Initially column J, a 2 meter silica gel column was used for separation. In order to improve on identification of organic acids this was later replaced by column R, a 1 meter column filled with ucon polyglycol LB-550-X.

EXPERIMENTAL RESULTS:

Gas Line: Because of leakages in the gas line and difficulties in the analysis of the individual absorbers, no interpretable results were obtained by this method. From the analysis of the material trapped by the dry ice - acetone bath nothing was observed. This was due mainly to the fact that the column used initially in the experiments, column J, did not show water peaks and any CO₂ trapped had vaporized and leaked away before analysis.

Graphs: All the graphs reproduced here were obtained by vapor phase chromatography (VPC) with the exception of part of graph #7. The background was always taken as 10 units vertical and this was also the starting point of each graph. All peak heights are times one (x1) unless otherwise specified. The multiplying factors appear above the graph at the peak noted. The small numbers appearing below the peaks

represent distances from the start for easy reference. Because of the nature of the recorder, the graphs always run from right to left. The data appearing in parenthesis below the title of the graph represents the column used, the column temperature, and the size of gas sampler or size of liquid sample introduced by syringe.

All sample temperatures given in the text of this report are the temperatures of the bath surrounding the decomposition flask at the time of sampling.

Run #1 = Glucose Alone (VPC - Column J - 100° - 0.25cc gas sampler):

Sample size = 10 grams of glucose

Sampling temperatures (°C) = 169, 191, 200, 224, 220, 232, 248, 255, 257

Nitrogen peaks = approx. 36 (x64)

Sample melting temperature = sample began to melt at about 165°.

Comments = With the first sampling at 169° a very wide diffuse band appeared (see graph #1A). CO₂ began to appear at 255° and 257° in small amounts (peaks = 6 and 4 respectively).

Run #2 = Glucose Alone (VPC - Column J - 100° - 0.25cc gas sampler):

Sample size = 10 grams of glucose

Sampling temperatures (°C) = 161, 171, 181, 191, 201, 211, 224, 234, 242, 251, 257, 268, 276, 287

Nitrogen peaks = approx 36 (x64)

Sample melting temperature = sample began to melt at about 160°.

Comments = With the first sampling the very wide diffuse band again appeared (see graph #1B). CO₂ began to appear at 251°

and continued to come off in small amounts up to the end (peaks = 0.5, 13, 3, 7, and 13 respectively)

Run #3 = Glucose + 20%(by weight) Anhydrous Na_2CO_3 (VPC - Column J - 100° - 0.25cc gas sampler):

Sample size = 10 grams of glucose + Na_2CO_3 mixture

Sampling temperatures ($^\circ\text{C}$) = 139, 153, 169, 175, 190, 220, 239

Nitrogen peaks = approx 35 (x64)

Sample melting temperature = sample began to melt at about 135° .

Comments = A high degree of bubbling due to the presence of

CO_2 was observed. CO_2 appeared with the first sampling and

large amounts continued to come off (peaks = 4, 84, 76 (x2),

68 (x2), 90, 52, and 78 respectively).

Discussion - (VPC - Column J): Using column J at 100° the wide diffuse band appeared in both runs of glucose alone but did not appear in the run of glucose mixed with Na_2CO_3 . In an attempt to identify these bands 87% formic acid, formaldehyde, acetaldehyde, and glacial acetic acid were each run through the column (see graphs #2A,B,C,D). Distilled water was also tried giving a graph such as graph #7. Only the glacial acetic gave the same type of band but with less height than those obtained in runs 1 and 2.

The boiling point of acetic acid is 118° . Since the column temperature was held at 100° the acid passed through as a liquid. As such, a sharp peak is virtually impossible to obtain and a broad diffuse band results. The behavior observed here could be expected for any substituent with a boiling point greater than 100° . It is quite likely that the decomposition products are low molecular weight organic sub-

stituents. Since simple aldehydes, alcohols, and ketones all boil at less than 100° it can reasonably be assumed that the band is due to acetic acid and any higher weight organic acids which may be present.

The melting temperatures of the sugar samples were lowered by about 30° with the addition of Na_2CO_3 . Temperatures above 250° were required to liberate CO_2 with glucose alone. However, CO_2 came off readily and in comparatively much larger amounts at temperatures as much as 100° lower when Na_2CO_3 was added. It has been observed that Na_2CO_3 dissociates to a very large extent when an aqueous solution of the salt is boiled (5). It is probable that the liberation of CO_2 may occur due to hydrolysis by the water produced on decomposition.

Distillation: An attempt was made to condense the decomposition products out of the system instead of passing the vapors directly into the VPC. The apparatus used (see drawing #3) was similar to that for the intermittent gas sampling, but a condenser and ice bath were added. A 5 gram sample of glucose alone was distilled and vapors collected over the range $160^{\circ} - 180^{\circ}$. This range was chosen because the wide bands observed in runs 1 and 2 appeared at 169° and 161° . A very small amount of liquid was obtained which was slightly acid to litmus.

A 10cc sample of the distillate was put through the VPC using column R at 150° . The graph obtained (graph #9) was very similar to that of distilled water (graph #7). A small bump appeared on the downward slope of the curve at 16 units.

This corresponds well with dilute propionic or extensively dilute acetic acid, the latter probably being the more likely because of the very weak acidic properties and low temperatures of the distillation.

Infrared Spectra: Infrared spectra were determined for the above distillate, glacial acetic acid, and 2N acetic acid on NaCl plates. These were compared with a spectrum of water in the literature (7). The distillate and 2N acetic produced spectra which agreed very closely with each other, but also agreed more closely with the water spectrum. This was to be expected since both the distillate and 2N acetic are mostly composed of water. Acetic acid did appear slightly in the graph of 2N acetic but not in the distillate graph. This could possibly be due to the extreme dilution of any acid present or to the presence of a different acid. Thus this attempt was inconclusive.

Infrared spectra were also determined on the distillation residue and on glucose, each finely ground and dissolved in Nujol, and on the Nujol itself. Absorption was very high for most of the range of the spectra, thus not permitting any conclusive results again.

Run #4 = Glucose Alone (VPC - Column R - 150° - 5.0cc

gas sampler):

Sample size = 7 grams of glucose

Sampling temperatures (°C) = 145, 165, 177, 186, 187, 195, 205, 215, 226, 236, 245, 257; 258, 265, 275, 285, 300

Nitrogen peaks = approx 70 (x128)

Sample melting temperature = sample began to melt at about 160°.

Observations = (see graphs 3A-K); 205°, the glucose sample began to bubble somewhat

215°, light white smoke began to be given off

226°, the sample began to turn black

Comments = At 257° the run was discontinued because of lack of time to continue. The sample was allowed to cool in the N₂ atmosphere. The run was restarted the next day at 258° with only a small lag in the succession of results.

Run #5 = Glucose + 10% (by weight) Anhydrous Na₂CO₃ (VPC - Column R - 150° - 5.0cc gas sampler):

Sample size = 7 grams of mixture

Sampling temperatures (°C) = 130, 145, 156, 167, 177, 185, 197, 205, 215, 225, 235, 244, 253

Nitrogen peaks = approx 70 (xl28)

Sample melting temperature = sample began to melt at about 130°.

Observations = (see graphs 4A-I); 130°, the sample began to puff up and turn brown. This was due to the CO₂ given off as shown by run 3.

177°, dark black splotches appeared in the melt. These were probably due to localized lowering of the melting temperature by Na₂CO₃ because of insufficiently thorough mixing.

Heavy bubbling also appeared.

185°, sample had turned almost completely black

Comments = At 197° vapor was condensing in the delivery tube and undoubtedly a small amount ran over the neck, down into the gas sampler and was introduced into the VPC as liquid rather than vapor, producing the unexpected curve (see

graph #4D).

Acids, Aldehydes, Ketones, Alcohols, CO₂ (VPC - Column R - 150° - 5.0cc gas sampler or 10_μl liquid): In order to identify the peaks appearing in the graphs of runs 4 and 5 and of the condensates presented later, graphs of various low molecular weight organic substituents were obtained. Acetaldehyde (freshly distilled), acetone, methanol, and ethanol all showed peaks at 2 units from the sampling points (graph #10A-D). When diluted 1:1 with distilled water these peaks either coincided with the water peaks or if displaced were masked by them and therefore did not appear. In any case the displacement could not have been more than a few units.

Since organic acids were suspected, the graphs of the four simplest of these were determined both concentrated and diluted 1:1 with distilled water (graphs 5A-D). Dilutions of 1:1 showed a displacement of about 2 to 3 units in each case. The exceedingly dilute acetic acid (or 2N) showed a further displacement of 2 units. This behavior can be expected for the other acids, too, the amount of further displacement increasing slightly perhaps with increasing molecular weight of the acids. The organic acids, unlike the other organic substituents tried, showed a broad downward sloping tail similar to that observed for water. In the higher molecular weight acids, as would be expected, various peaks occur between the water and acid peaks. These represent impurities or decomposition products of the acids.

HCl was added to NaHCO₃ in a flask previously flushed with N₂ and the CO₂ generated was sampled in the VPC. The

resulting graph (graph #8) showed a peak at 3 units. The small amount of CO_2 compared with N_2 can be attributed to failure to generate enough CO_2 to completely drive out all the N_2 prior to sampling.

Discussion of Glucose and Glucose- Na_2CO_3 Runs (VPC - Column R) - Runs 4 and 5 : With these two runs a 5.0cc gas sampler was used in place of the 0.25cc sampler. The sensitivity of the determinations was considerably increased. Great care was also taken in stirring the silicone bath in these experiments, a precaution not taken previously. This insured that the temperature recorded as the sampling temperature was the true temperature of the bath. A drop of $10 - 15^\circ$ in the thermometer reading on stirring was often observed. In addition, the presence of Na_2CO_3 in the glucose samples again lowered the melting temperature by 30° .

The sharp peak appearing at 6 units from the sampling point, and followed by a broad downward slope was observed in the N_2 line, air, and all gas samples. It is attributed to water vapor. The large displacement from 2 units is due to the large preponderance of N_2 present in the sample and the small amount of water vapor.

In the case of the run on glucose alone, there is a significant decrease in the height of the water peak at 186° (graph #30) and 195° for some reason. It returns to its former height at 205° , the same temperature at which bubbling began. This peak again increases from 265° on up (graphs 31-K). Fairly large peaks appear in the vicinity of 275° to 285° . With the run on the glucose- Na_2CO_3 mixture, ignoring

the 197° sampling, large peaks occurred in the vicinity of 215° (graphs #4E-G).

In both runs a series of peaks appeared at 3 and 4 units. In the run of glucose alone these both began to appear together at about 257° and continued to increase in size up to the end of the run. In the case of the glucose- Na_2CO_3 mixture the peak at 4 units began to appear with the first sample at 130° and that at 3 units at 197°. Neither were very large except from 177° to 197° (graphs #4C-D). The appearance of the peak at 4 units corresponds roughly in both cases to the behavior of CO_2 determined with column J earlier in the experiment. The peaks at 3 units could well correspond to aldehydes, ketones, and alcohols of low molecular weight. In both cases they would show a deviation of 1 unit from the peaks obtained in graphs #8 and #10A-D.

With the run of glucose alone a "bump" appeared on the graph at about 19½ units at 215° (graph #3D). This continued in varying but significant heights up to the end of the experiment. From 265° to 285° (graphs #3H-J) it was supplemented by another peak at 17½ units. In the glucose- Na_2CO_3 run which followed immediately, this bump also appeared in the N_2 line, perhaps due to some residue remaining in the gas sampler (graph #4A). This bump was almost nonexistent for the entire run. It was also supplemented by another bump at 12½ units from 205° to 225° (graphs #4E-G).

Condensates from Runs 4 and 5 (VPC - Column R - 150° - 10.1): During the run of glucose alone, run 4, some of the vapors had condensed in the gas sampler. Immediately follow-

ing completion of the run this condensate was allowed to drip out of the sampler and was collected. In the case of the glucose- Na_2CO_3 run, run 5, this condensate was collected in a similar manner following the sampling of a slug of condensed vapors carried over to the sampler at 197° . The pH of the condensates were tested with Hydrion paper and found to be between 2 and 3 -- moderately to weakly acidic. Graphs of each condensate were obtained on the VPC (graph #6).

The triangles in graph 7 are a representation of peak distances from the sampling point appearing for the four acids, concentrated and dilute 1:1, and superimposed on a graph of distilled water. These are placed on the same time scale as the condensate graphs appearing above it for comparison.

Water was by far the largest constituent of both condensates. As seen from the representative acid peaks in graph #7, the first acid peaks appearing in the condensate graphs at 11 units represent formic acid, the second at 13½ - 14 represent very dilute acetic acid, the third at 18½ represent very dilute propionic acid. The acetic and formic acid peaks in graph #7 are similar only because the "concentrated" formic acid has already been diluted to 87%. The fifth peaks appearing at 33½ units only roughly approximate butyric acid; the fourth at 25½ did not seem to correspond to anything which was tried.

The acid peaks appearing in the condensate from the glucose alone run were up to two times higher than those appearing for the other. This difference was most marked for pro-

pionic acid, less so for acetic, and the peaks were almost equal for formic. It appears possible that the presence of Na_2CO_3 might tend to cause decomposition of the sugar into lower molecular weight acids, and at lower temperatures. Since lower molecular weight substituents appear sooner than their heavier counterparts as with the acids, the appearance of peaks at 19% and 17% units with glucose alone but at 19% and 12% units with the glucose- Na_2CO_3 mixture might be explained.

Acid Flammabilities: Samples of 87% formic acid, glacial acetic, and propionic acid were placed in watch glasses and exposed to a Bunsen burner flame. The formic acid did not burn. The glacial acetic acid burned only weakly with a blue flame and went out rather easily. The propionic acid burned easily and with a more yellowish flame. In addition, cubes of lump sugar (sucrose) were dipped in each of these acids and exposed to a Bunsen burner flame. The observations on the cubes was exactly the same as for the acids themselves.

Sugars and Catalysts: Approximately 10% of various catalysts were mixed with various sugars. A small amount of this mixture was placed on a nickel spatula, thrust into a Bunsen burner flame and the action observed.

	no catalyst(a)	Na_2CO_3 (b)	$\text{NaC}_2\text{H}_3\text{O}_2$ (c)	HgCl_2	CCl_4 (d)
sucrose	-	+	+	+	+
glucose	-	-	+	+p	
fructose	-	+	+		
lactose		+p			
maltose		+p			
galactose		-			

+ represents that burning was observed, +p represents that burning was very weak, - represents that burning was not observed. (a), The sugar bubbled vigorously and much boiled away before the residue burned at very high temperatures. (b), With Na_2CO_3 a sort of moist foaming occurred when placed in the flame whether or not combustion occurred. (c), Using $\text{NaC}_2\text{H}_3\text{O}_2$, black bubbles formed and a black porous foam snaked out during the combustion. (d), A strong shooting of flames out from the sample occurred during combustion.

The effect of Na_2CO_3 on the sugars varied from no or very little effect with glucose and galactose, through slight tendencies to burn with maltose and lactose, to vigorous combustion with sucrose and fructose.

Discussion: One of the problems in interpreting data of the type sought in these experiments is the difficulty in identification of peaks obtained with the VPC. Even using the same column and column temperature the displacement of a peak, because of dilution or the presence of other substituents, makes it difficult to pinpoint products accurately. Peaks therefore generally can be said to fall in a certain range, the most probable of which depends upon its concentration in the sample.

In the article by Ambler and Byall referred to earlier (1), three classes of non-sugar effects were given. Class 2 compounds which include salts which react alkaline and salts of strong bases with volatile acids and class 3 compounds which include NH_4^+ salts, amino acids, and iron salts have been shown to catalyze the combustion of sucrose. According

to Ambler and Byall both these classes increase the caramelization of a sucrose solution. There is a strong likelihood that these two processes have a distinct relationship with one another.

In the present series of experiments formic, acetic, propionic, and possibly butyric acids were observed in the decomposition products of glucose along with water as the major constituent. The presence or absence of other low molecular weight organic substituents such as aldehydes, ketones, and alcohols was not determined for sure because of the masking effect of water and the poor resolution of the columns between them. But for the runs of glucose and glucose- Na_2CO_3 mixtures, runs 4 and 5, small peaks appeared which probably were due to the presence of these substituents among the decomposition products. The acids were, however, a ready source of H^+ which with the water of decomposition might feasibly take part in the reaction or cause the catalytic effect. In the article by Ambler and Byall mentioned above and also in an article by Pucherna (6) it is mentioned that the acidity of a sucrose solution increases with increasing temperature. If these acids are also given off by sucrose upon decomposition, the H^+ might tend to cause inversion of some of the unreacted sucrose to glucose and fructose. The presence of any alkaline additive such as Na_2CO_3 would of course reduce or negate the H^+ concentration. Acidic additives such as NH_4^+ salts and chlorides probably have a totally different mechanism when catalyzing the combustion of sugars.

It was further observed that in the graphs of the con-

condensates, the ratio of amounts of organic acids given off with and without catalyst followed a trend. Thus it is also possible that Na_2CO_3 could cause a tendency for decomposition into greater amounts of lower molecular weight organic acids. How the Na_2CO_3 affected the other organic substituents such as aldehydes, ketones, and alcohols which may have been given off could not be determined. Higher molecular weight acids, i.e. propionic, are easier burning than lower ones such as formic. The presence or absence of aldehydes, ketones, and alcohols which are much more combustible probably make more of a difference in the catalytic action of these additives.

Because of the nature of sampling of the condensates, the results obtained from them are open to question and any explanations based on them do not stand on the firmest ground.

The original problem dealt with the action of various catalysts on sucrose. In an attempt to simplify the question of decomposition products and mechanism a simple sugar, glucose, was selected to be studied in this series of experiments. Because of this and other differences observations on glucose decomposition cannot validly be applied to explanation of the combustion of sucrose, a much more complicated sugar. However, this represents a start in the determination of the decomposition products of sugars which it is hoped will eventually lead to discovery of the mechanism of the combustion of sucrose.

SUGGESTIONS FOR FURTHER WORK:

Considerably more work must be done and much more organized data must be obtained before an attempt is made to con-

clusively explain the catalytic action in the combustion of sugar. It is suggested that samples of glucose and glucose- Na_2CO_3 be distilled in a nitrogen atmosphere over a full range from melting to $250^\circ - 300^\circ$ instead of 160° to 180° as was done in these experiments. The distillates collected should be passed through column R at 150° to identify acid and another column better capable of resolving any aldehydes, ketones, and alcohols present from water. Distillates can also be collected over small temperature ranges for determination of temperature dependence on the products. Column temperatures should be kept above the boiling points of expected decomposition products to avoid any long delays in resolution or broad diffuse peaks or bands.

Glucose, fructose, sucrose, and other sugars can be distilled with and without a series of different catalysts of different classes under the same conditions as above and their distillates collected and passed through various VFC columns.

Intermittent gas sampling may still be used as in the present series of experiments to determine products if a helium carrier was used to remove the large initial peak due to nitrogen carrier. The helium would not appear in the graph because it is also the gas used in the operation of the chromatograph. Coupled with a different column which showed better resolution of light organic substituents, these results might also prove fruitful.

SUMMARY:

In order to add information for an explanation of the

catalytic combustion of sugar, experiments were carried out to determine the identity of the decomposition products of glucose. Glucose was preferred to sucrose because it was thought that the decomposition products might be simpler. Na_2CO_3 was the catalyst used because of its large effect. The decomposition products were in general sampled directly from the decomposition flask as vapors by vapor phase chromatography. These were checked against knowns for identification. Infrared spectrometry was tried for identification of the distillate products but did not prove very successful.

The melting temperatures of the glucose were lowered by about 30° due to the presence of Na_2CO_3 in the sample. Generally reaction temperatures were also similarly lowered 30° to 70° for appearance of some peaks. The major decomposition product was water. CO_2 was given off by glucose alone above 250° . In the case of mixtures of glucose and Na_2CO_3 the CO_2 appeared right after the glucose melted at 130° due probably to the action of water of decomposition on the Na_2CO_3 .

Condensates were collected for two such runs. Each had a pH of between 2 and 3. Formic, acetic, and propionic acids, and possibly butyric were found in these condensates. Less acid was found in the run on the glucose- Na_2CO_3 run relative to the run on glucose alone. Propionic acid was found to burn well, acetic acid weakly and went out easily; formic acid did not burn at all. The higher the molecular weight the more readily the acid burns. Other organic substituents such as aldehydes, ketones, and alcohols which are far more combustible than the acids were probably present but amounts and identifi-

cation were not determined because of the poor resolution with these compounds of the columns used.

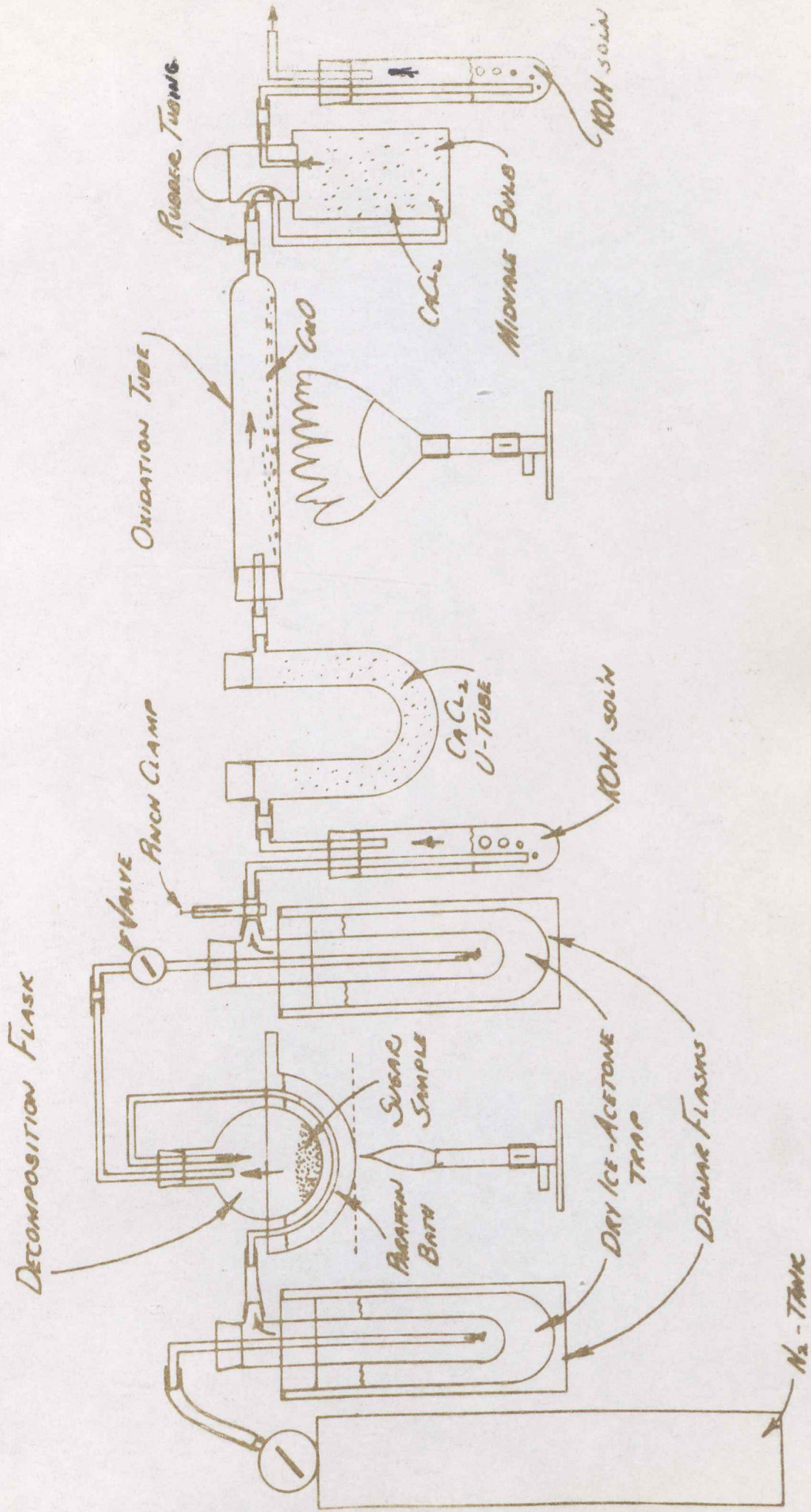
Speculations on possible mechanisms include; 1- the action of H^+ with water of decomposition to invert portions of unreacted sugar (sucrose) to glucose and fructose. This would be prevented or hindered by the presence of an alkaline catalyst, causing different starting sugars for decomposition processes. If inversion occurred, glucose and fructose would be decomposing; if inversion was prevented, the decomposition would occur directly from the sucrose without going to the invert sugar step. 2- the action of Na_2CO_3 in tending to form larger amounts of lower molecular weight organic acids in the decomposition products. 3- the presence of aldehydes, ketones, and alcohols among the products which, if different in amount and type with and without catalyst, would probably have a greater effect on combustion than the acids.

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#1

GAS LINE



INTERMITTENT GAS SAMPLING

#2

VAPOR PHASE CHROMATOGRAPH

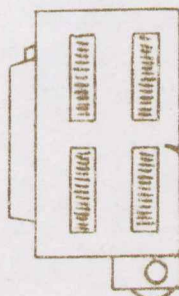
GAS SAMPLING VALVE

DELIVERY TUBE

DECOMPOSITION FLASK

TRAP

#22 NICHROME WIRE HEATER
ENCASED IN PYREX TUBING
SILICONE OIL BATH



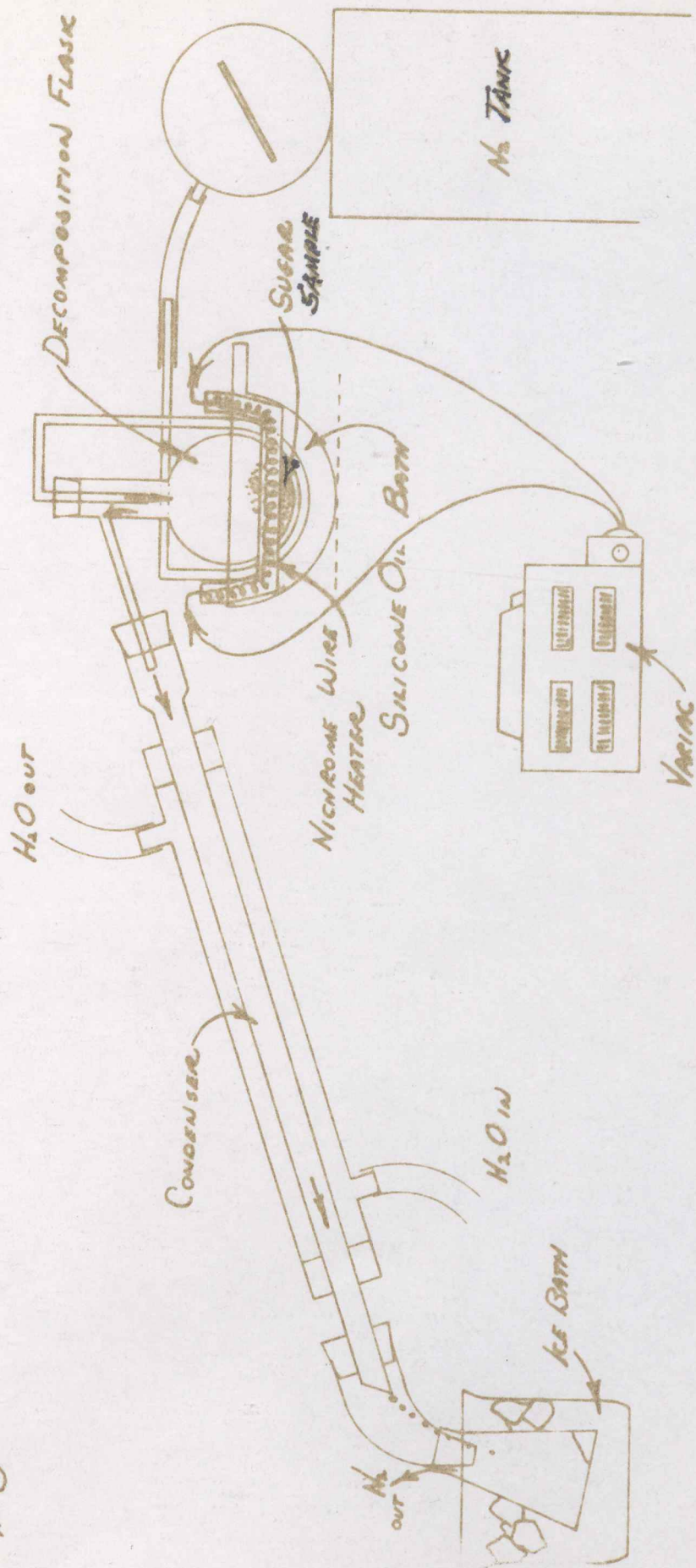
VARIAC

N₂ TANK

BUBBLE COUNTER

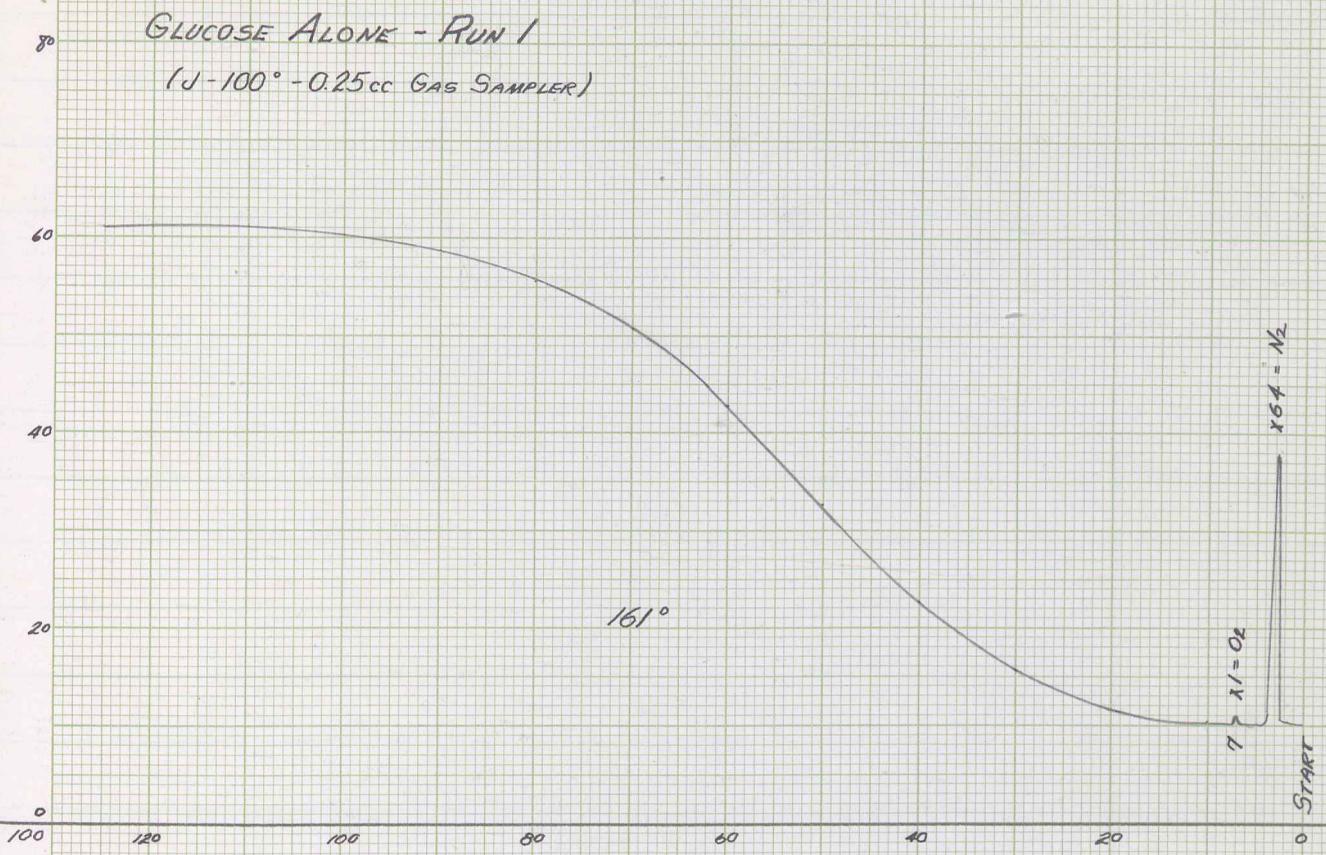
DISTILLATION

3



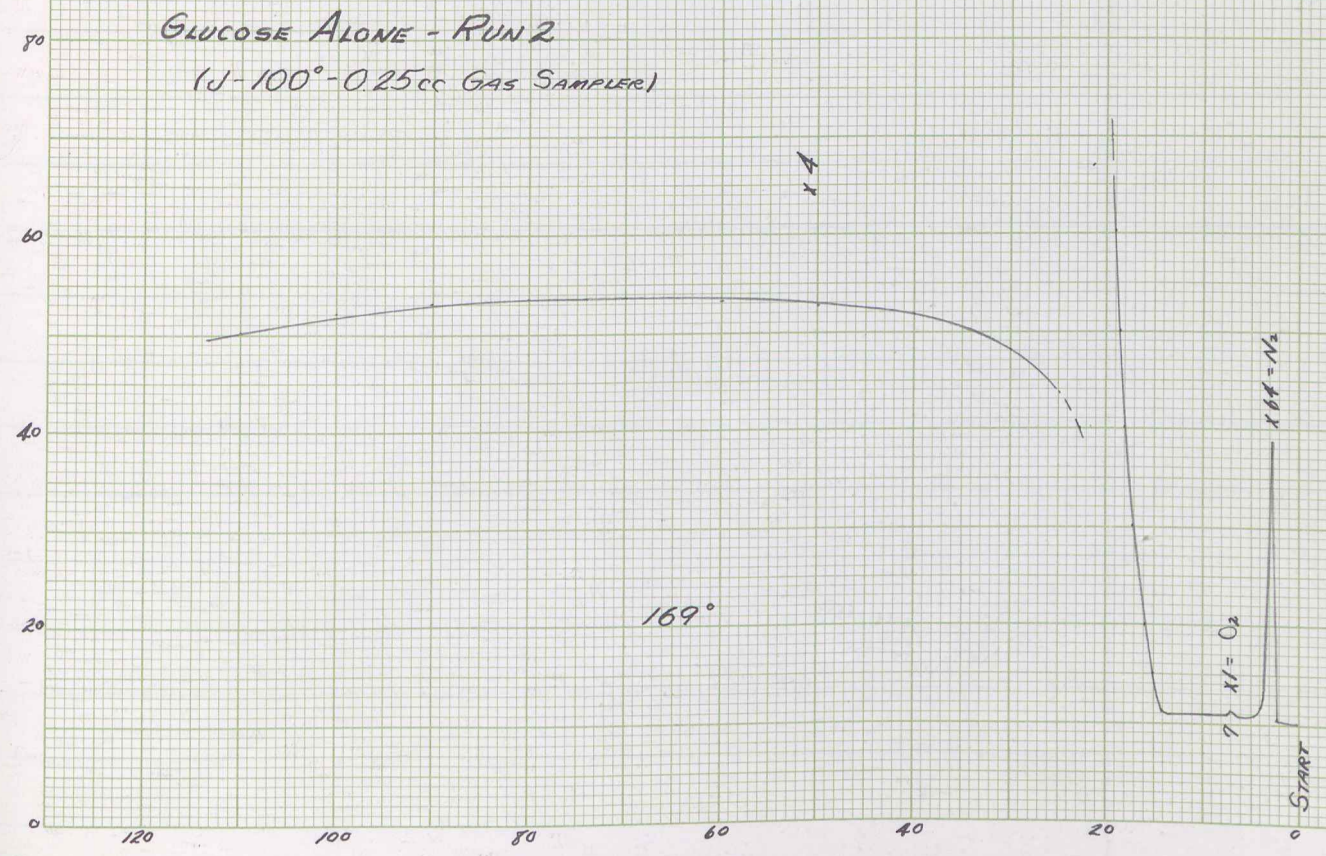
#1/A

GLUCOSE ALONE - RUN 1
(J-100° - 0.25cc GAS SAMPLER)



#1/B

GLUCOSE ALONE - RUN 2
(J-100° - 0.25cc GAS SAMPLER)



#2C

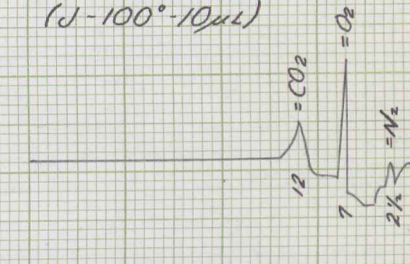
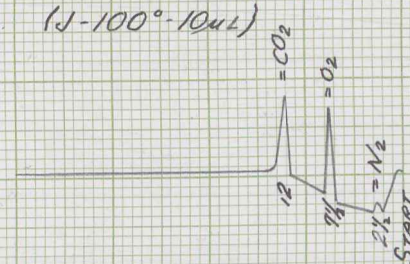
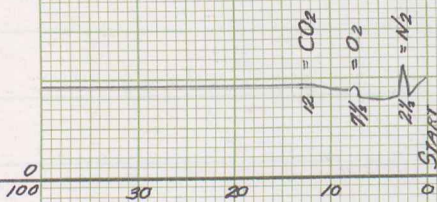
#2B

#2A

ACETALDEHYDE
(J-100°-10μL)

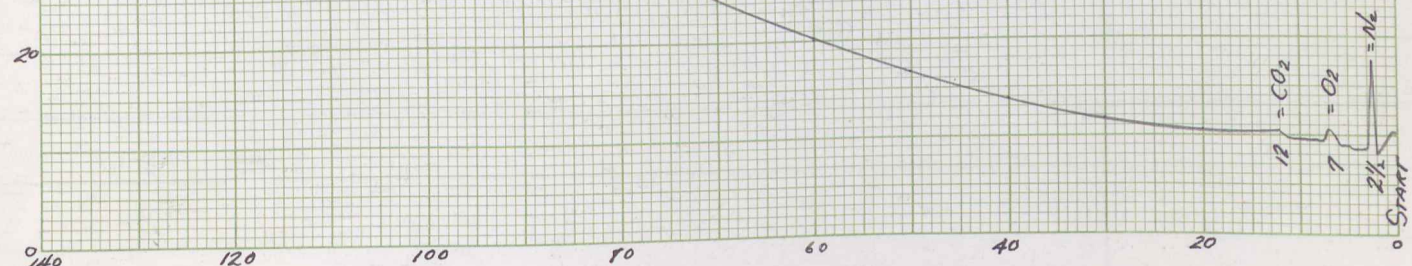
FORMALDEHYDE
(J-100°-10μL)

FORMIC ACID
(J-100°-10μL)

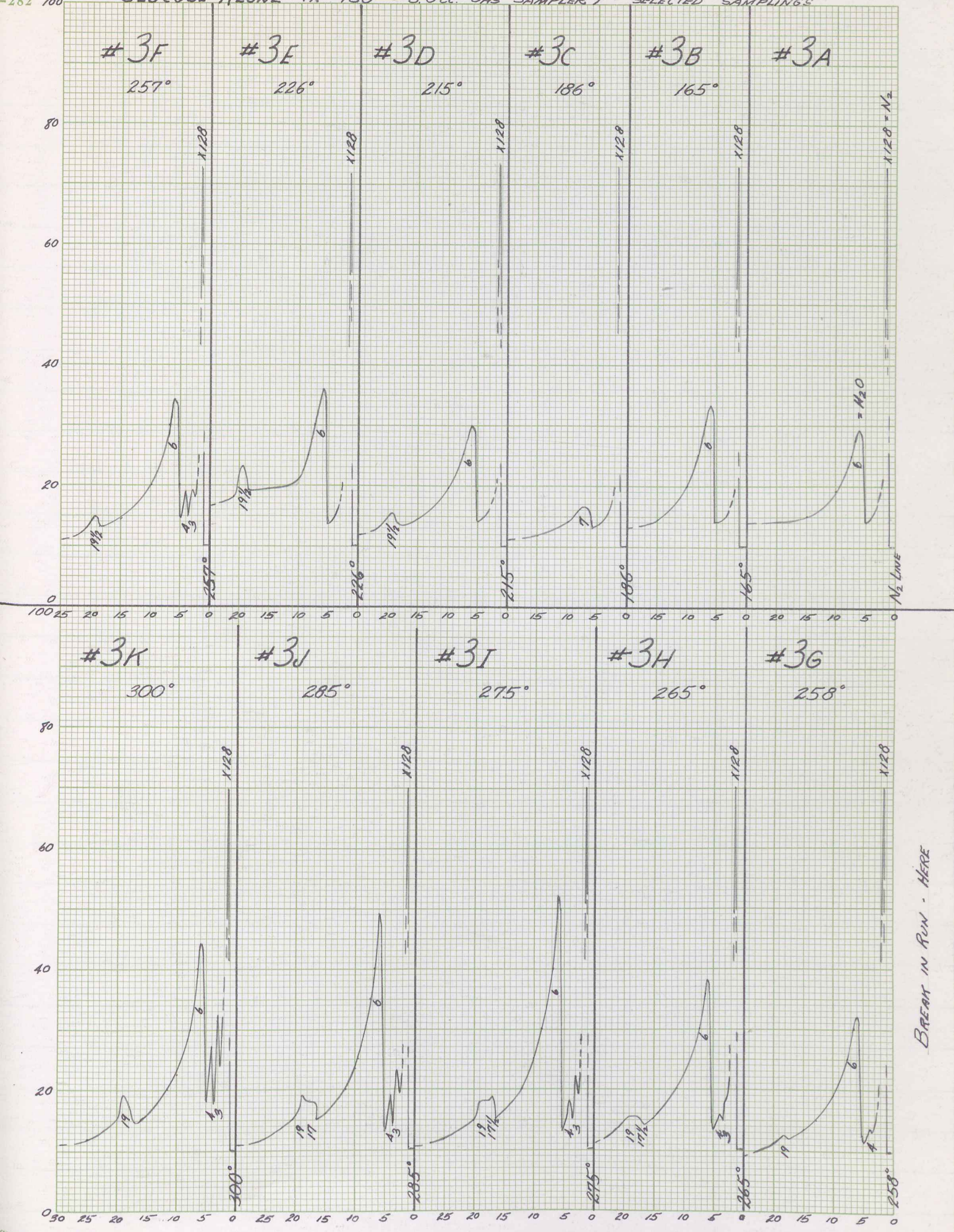


#2D

GLACIAL ACETIC ACID
(J-100°-10μL)

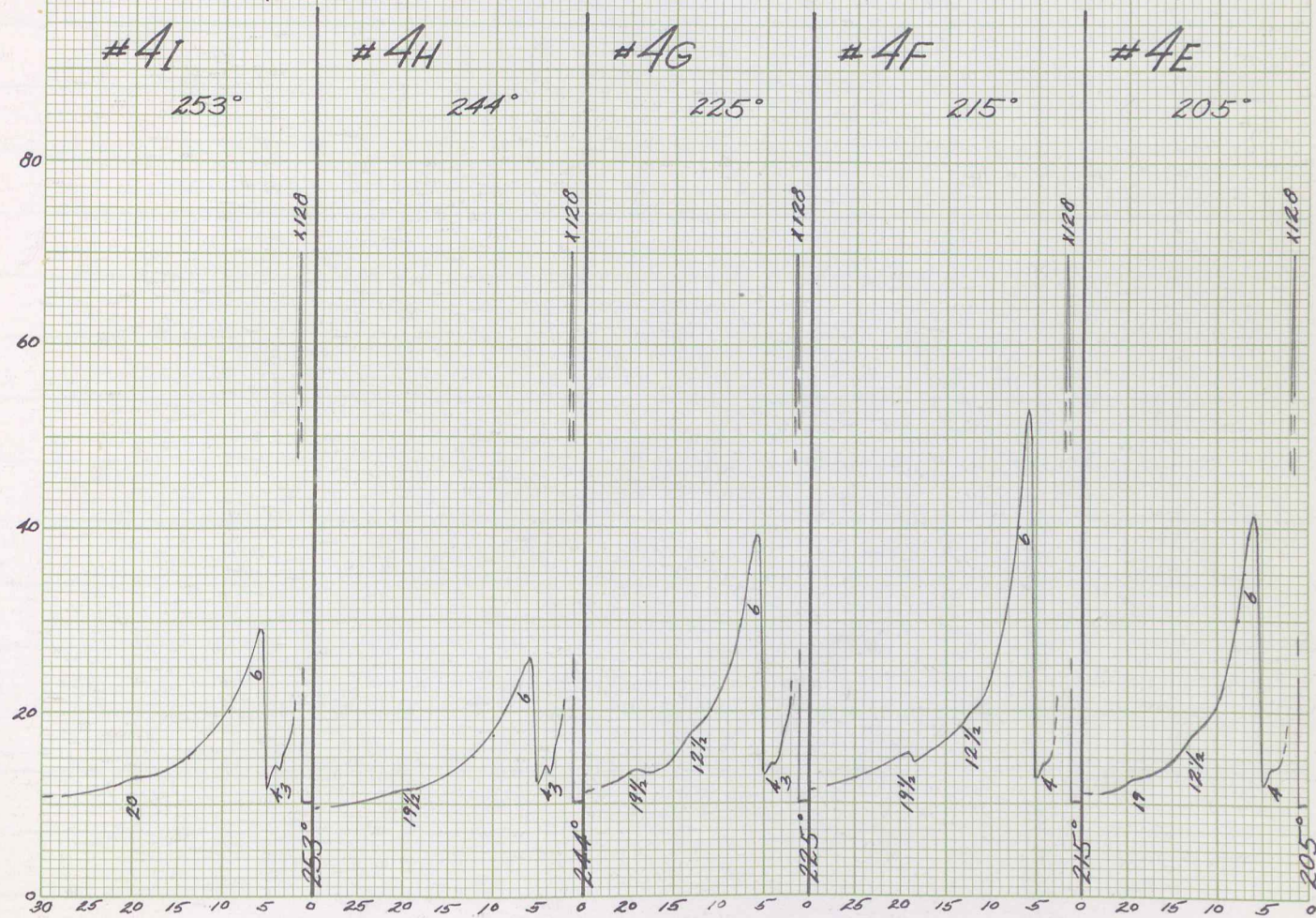
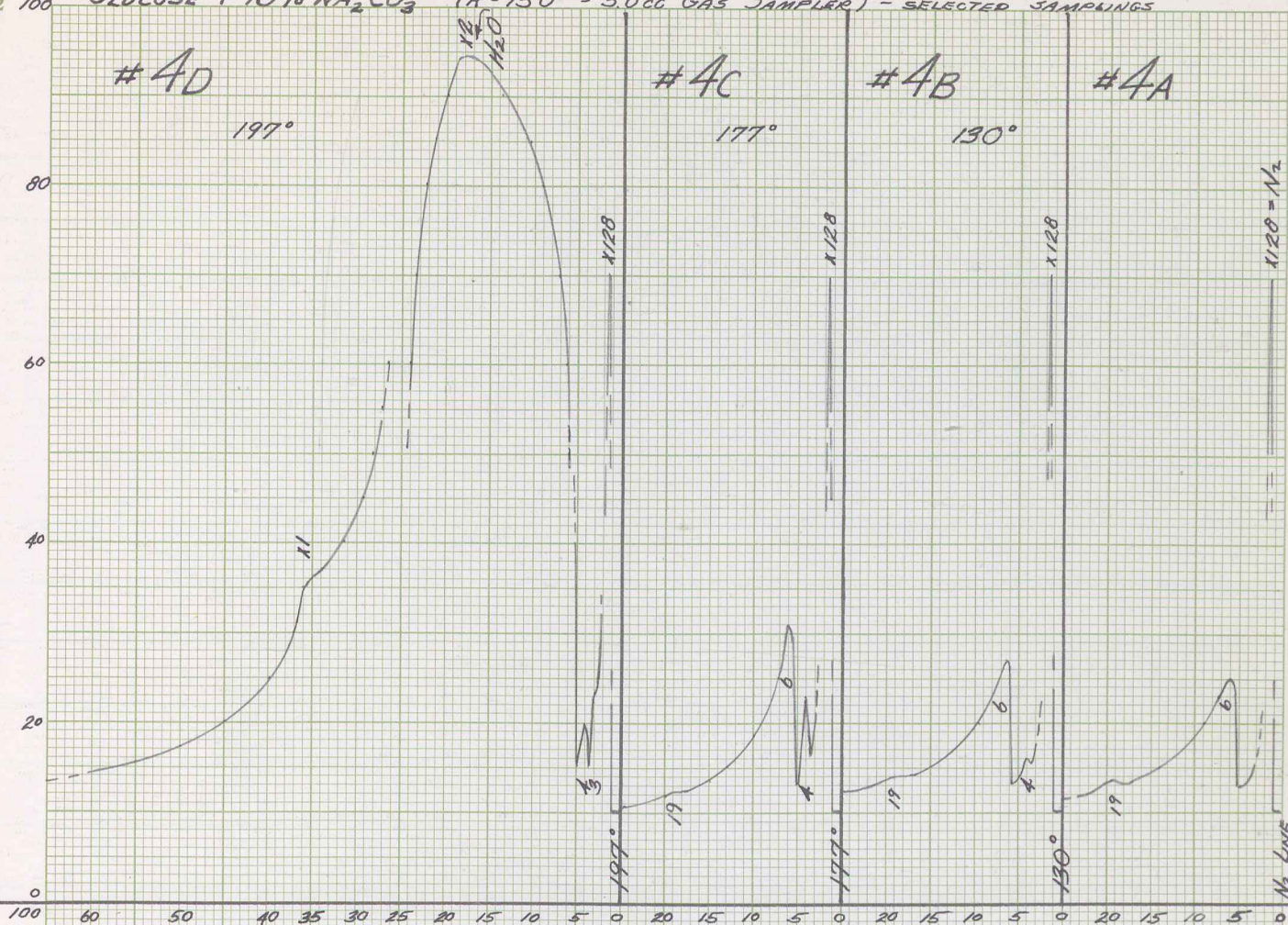


GLUCOSE ALONE (R-150° - 50CC. GAS SAMPLER) - SELECTED SAMPLINGS



BREAK IN RUN - HERE

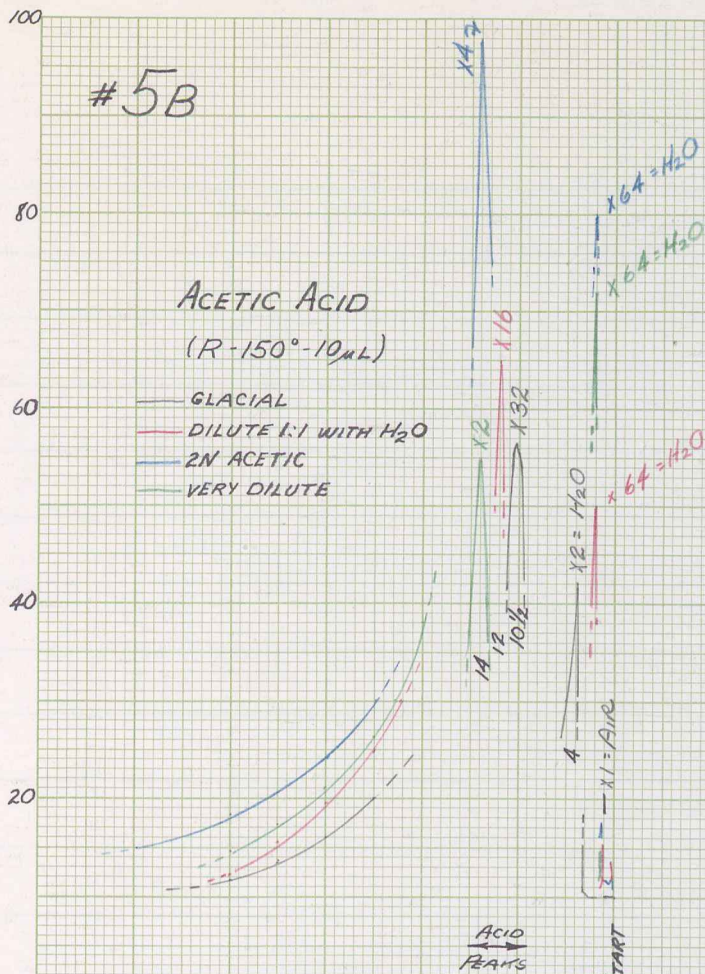
GLUCOSE + 10% Na_2CO_3 (R-150° - 5.00G GAS SAMPLER) - SELECTED SAMPLINGS



#5B

ACETIC ACID (R-150°-10μL)

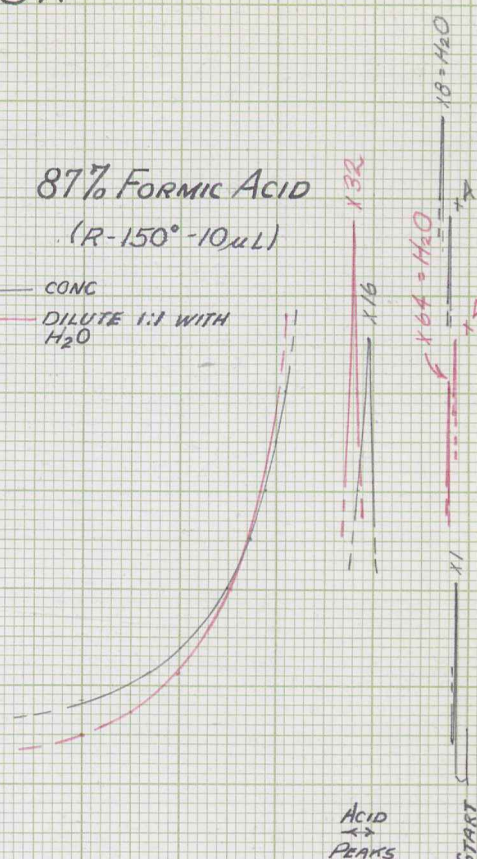
- GLACIAL
- DILUTE 1:1 WITH H₂O
- 2N ACETIC
- VERY DILUTE



#5A

87% FORMIC ACID (R-150°-10μL)

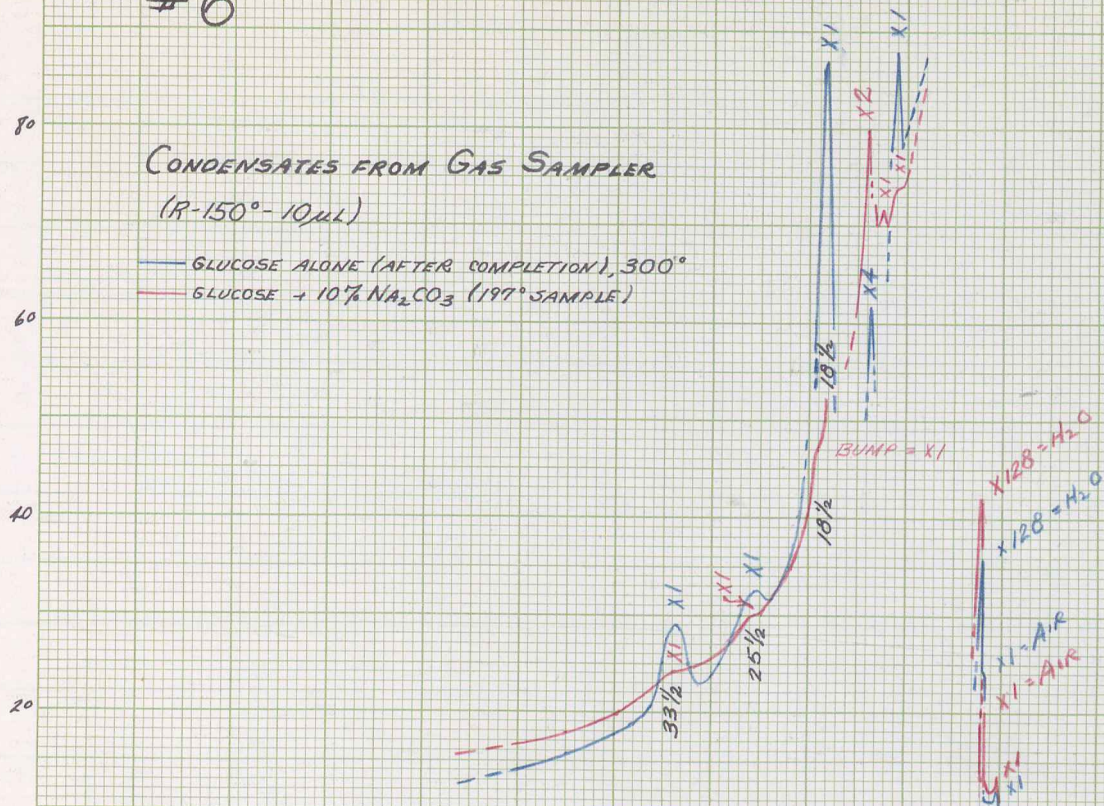
- CONC
- DILUTE 1:1 WITH H₂O



#6

CONDENSATES FROM GAS SAMPLER (R-150°-10μL)

- GLUCOSE ALONE (AFTER COMPLETION), 300°
- GLUCOSE + 10% Na_2CO_3 (197° SAMPLE)

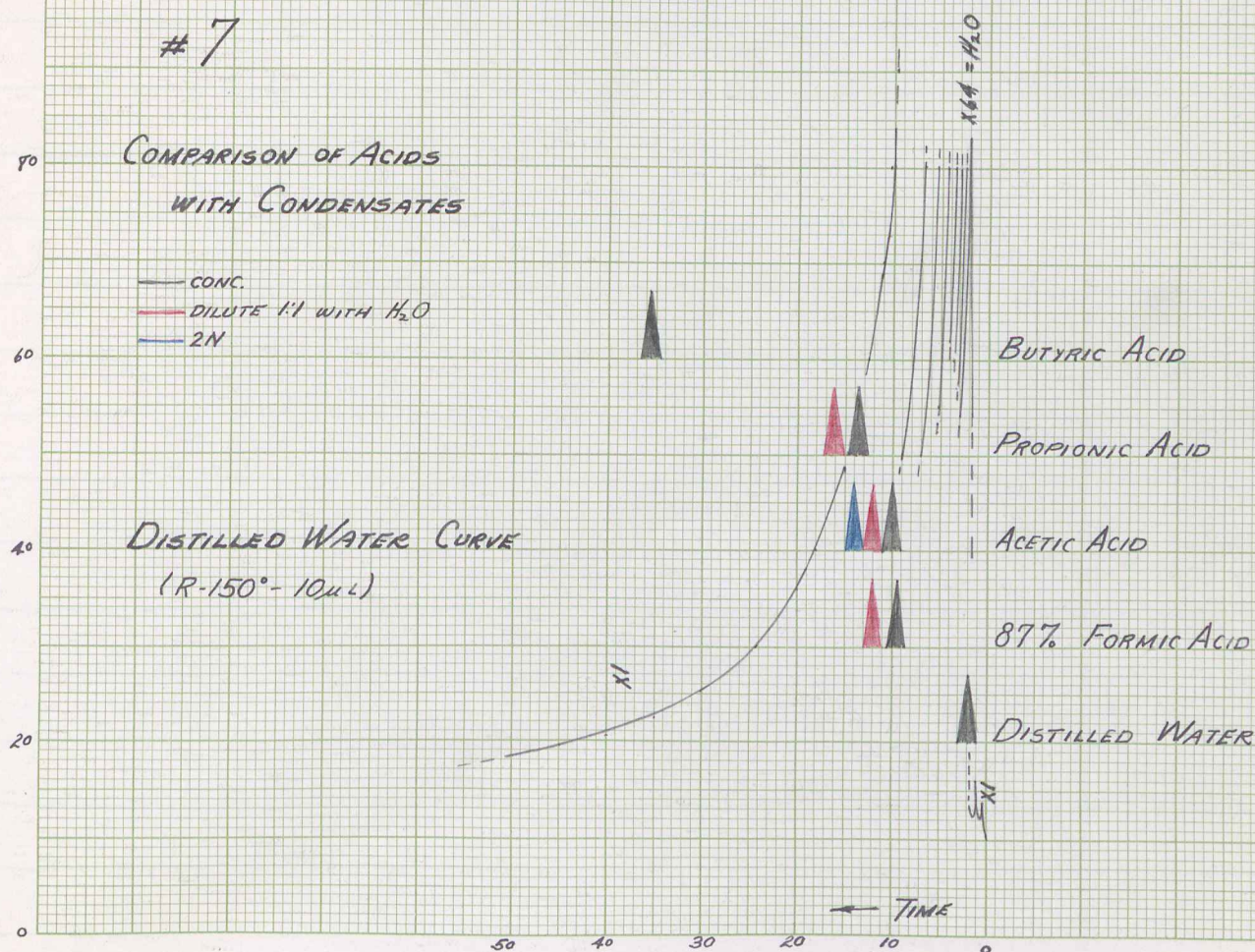


#7

COMPARISON OF ACIDS WITH CONDENSATES

- CONC.
- DILUTE 1:1 WITH H_2O
- 2N

DISTILLED WATER CURVE (R-150°-10μL)



#9

DISTILLATE, 160-180°
GLUCOSE ALONE
(R-150°-10uL)

80

60

20

0

x64 = H₂O

START ——— AIR

#8

CO₂
(FROM NaHCO₃ +
HCL IN N₂ LINE)
(R-150°-5.0cc
GAS SAMPLER)

x128 = N₂

x1 = CO₂

START

#10D

ETHANOL
(R-150°-10uL)

x64 = ETHANOL

x12 = H₂O

x1

1/16 x1 = AIR

START

#10C

METHANOL
(R-150°-10uL)

x128 = METHANOL

x1

x1 = AIR

START

#10B

ACETONE
(R-150°-10uL)

ACETONE
x164

12 1/2

6 1/2

5

2

x1 = H₂O

START

#10A

ACETALDEHYDE
(DISTILLED DIRECTLY
FROM PARALDEHYDE
+ ACID, CARRIED
IN N₂ LINE)
(R-150°-5.0cc
GAS SAMPLER)

x12 = ACETALDEHYDE

x128 = N₂

6

3

x1 = H₂O

START