

THE ESTIMATION OF THE PENTOSE:

- I. THE FORMATION AND DISTILLATION OF FURFURAL
- II. THE DETERMINATION OF FURFURAL

A Thesis

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I. THE FORMATION AND DISTILLATION OF FURFURAL

INTRODUCTION

That the wide distribution of the pentosans in nature, as pointed out by Tollens in 1891, may be of considerable significance in plant economy is indicated by the work of Spoehr (1919), Hooker (1920) and Rosa (1920). These substances also constitute a large portion of the nitrogen free extract of many animal feeds and have been the subject of numerous experiments in animal metabolism. (McCollum and Brannon (1909), Swartz (1911)). The pentosan determination has also been used as a basis for determining the degree of milling of flours (Gerum (1920)). It is apparent, then that a convenient and accurate method for estimating these substances is very necessary. Because of the serious shortcomings inherent in the official method for determining pentosans, the present work was undertaken.

HISTORICAL

Formation of Furfural

Döbereiner (1832) first obtained furfural by the distillation of sugar with pyrolusite and sulfuric acid. Stenhouse (1840) later showed the pyrolusite to be unnecessary, while Völckel (1853) found that furfural was a decomposition product of many carbohydrate materials. Stenhouse (1850) was the first to prepare furfural on any appreciable scale. He distilled wheat bran with strong sulfuric acid. The use of a strong solution of zinc chloride in the distillation procedure was proposed by Babo (1853). Stone and Tollens (1868) and Wheeler and Tollens (1869) used sulfuric acid of various concentrations. Phosphoric acid was tried by Mann, Krüger and Tollens (1896). Glacial acetic acid was used by Testoni (1917). It was early recognized, however, that the use of 12 per cent hydrochloric acid gave better yields of furfural, in a shorter time, with more accurate duplication of results, and with less charring, than when any other acid was used (Allen and Tollens (1890), Günther and Tollens (1890), de Chalmot and Tollens (1891), Counselor (1892), Stone (1897), Hauers and Tollens (1903), Jolles, (1905), Ling and Hanji (1921)). Moreover, even acid of 12 per cent concentration has an appreciable destructive effect on furfural as shown by Fraps (1901), Jolles, (1905), Mayer and Tollens (1907) and van Hearst and Olivier (1914) and also upon pentose as argued by Unger and Jäger (1903) and Fraps (1915). Also, araban and fucosan, as

well as the corresponding sugars, produce furfural very slowly so that the yield from them is lower than that from others of the group due to the destructive action of the acid as has been shown by the above writers and by Kunz (1916). The yields of furfural usually obtained are recorded in Table I.

Substances other than pentose may also yield furfural on distillation with acid. Glucuronic acid is one of these and Tollens (1909) has determined it by a method identical with that for pentoses. However, glucuronic acid is rarely encountered. It has also been claimed that oxycellulose produces furfural. This statement appears to be based on the early work of Cross, Bevan and Beadle (1894), Vignon (1899) and Faber and Tollens (1899) which was done before the production of hydroxymethylfurfural from hexose materials was established. Moreover, much of the furfural said to be produced from cellulose may really have its origin in true pentosans ("hemi- and ortho-pentosans") contained in the cellulose. (König and Rump (1914), Schwalbe (1918), Heuser and Haug (1918) Schwalbe and Becker (1920)). Other interfering substances have been mentioned, but little is known concerning their composition and distribution. Bray and Staidl (1922) claim to have worked out a correction to lessen the error due to these substances but have not published it.

Table I

Yields of Furfural Obtained from Pentose Materials by
Distillation with Acid

Material	Yield, per cent.	Observer.
Arabinose	48	Browne (1912)
"	47.56	Unger and Jäger (1903)
"	47.7 - 52.7	DeChalmot and Tollens (1891)
"	57.	Mackenzie (1914, p.147)
Arabinose and Xylose	50 - 52	Hotter (1893)
" " "	50	Günther and Tollens (1890)
Xylose	57.50	Unger and Jäger (1903)
"	57.60	Browne (1912)
"	56 - 59	DeChalmot and Tollens (1891)
Pentosans	50	DeChalmot (1894)
Pentoses	54.4	Ling and Nanji (1921)
"	64	Jolles (1905)
Pentoses	64	Theoretical

Tests for Furfural

For determining when distillation is complete, aniline acetate has usually been used. This is prepared by adding glacial acetic acid to a mixture of equal parts of colorless aniline and water until the mixture suddenly clears. It has been frequently observed, however, that acetic acid often gives a positive test, due to the presence in it of furfural, as was shown by V. Meyer (1878). To avoid the difficulty, the use of concentrated hydrochloric acid has been recommended by Tolman and Trescott (1906), Cumingham and Doree (1914) and Schorger (1917). But strong mineral acids may destroy the color as has been argued by de Chalmot (1893) and by Baker and Hulton (1916). Hydroxymethylfurfural, arising from hexoses during acid distillation, does not interfere since it is formed so slowly and in such small quantities (van Ekenstein and Blanksma (1910), Cuningham and Doree (1914)). Jolles (1905) believed the aniline test was not sufficiently sensitive, and used Bial's orcinol- ferric chloride test solution. Van Haarst and Olivier (1914) preferred phloroglucinol. The present official method for the determination of pentoses makes no mention of the use of an indicator. Distillation is simply carried out at a definite rate until a definite volume of distillate has been received.

THE PRESENT OFFICIAL METHOD

The official method of distillation is to heat the sample with 12 per cent hydrochloric acid at such a rate that 30 cc. pass over in 10 minutes. Another 30 cc. of 12 per cent acid are then added and the process repeated until 12 fractions have been received.

The following modifications have been proposed:

Cross, Bevan and Smith (1895) suggested the use of the constant level apparatus of Chorley (1895) and Stanek (1900) devised an automatic apparatus to facilitate the procedure but these have not come into use. Heuser (1921) found that higher and more accurate yields of furfural were obtained if the weighed sample of pentosan was dissolved in normal sodium-hydroxide solution before distilling with acid. Dekker (1914) added 500 cc. of 12 per cent HCl and distilled directly. His results were low. Grund (1902) added and distilled in 50 cc. fractions and recorded a more intensive action by the change. Jolles (1905) added the acid, and steam distilled the hydrolysate, heating the latter so that its volume decreased to about half while 800 cc. of water were distilled through it. More acid was then added and the process repeated until no more furfural was produced. Jolles claimed to get theoretical conversions of pentose to furfural, the only such claim made in the literature.

EXPERIMENTAL

Materials used. The following pentose materials were used:

l-Arabinose, $[\alpha]_D^{20} = 103.77^\circ$

d-Xylose, $[\alpha]_D^{20} = 18.81^\circ$

As pentosan containing materials, pine sawdust and gum arabic were used, each being ground to 50 mesh size. These materials were distilled with acid according to the procedures outlined below and the furfural containing distillate titrated by the method proposed in Part II which is briefly as follows:

Method of determining furfural. A small aliquot of the distillate was titrated with standard alkali to determine its acidity. This aliquot was then readded to the distillate and sufficient HCl or strong NaOH solution also added to give a final acidity of about 4 o/o. 10 cc. of 20 per cent KBr was then added and the resulting solution titrated with standard $KBrO_3$ solution in the manner described in Part II.

Indicator used. For deciding when distillation was complete strips of filter paper were used which had been dipped in aniline hydrochloride solution and dried. The aniline hydrochloride solution was prepared from colorless aniline and C. P. hydrochloric acid.

Effect of Acidity During Distillation

Due to the ease with which furfural is destroyed by strong acid, a study of the acidities obtained during distillation was regarded essential. Two 12 per cent HCl distillation procedures were studied, (1) the method of the Association of Official Agricultural Chemists (1920), which has been said to yield low furfural figures, and (2) the method of Jolles in which theoretical yields were claimed. In both studies the boiling point temperatures were taken as an index to the concentration of acid present in the distillation flasks.

Official distillation procedure. The samples were distilled with 100 cc. of 12 per cent HCl at such a rate that 30 cc. passed over in 10 min. 30cc. more HCl was then added and the process repeated until no more furfural was produced. In each instance the distillation began at 103-104° but had reached 108.55° (cor.) by the time 60 cc. had been distilled out. Subsequent additions of 12 per cent HCl caused a temporary drop of 0.6° but the constant boiling temperature was very soon again reached. The greater part of the distillation took place therefore from acid of 18-20 per cent concentration. The data are recorded in Table II.

TABLE II.

Pentose Distillations by the Official Method

Material.	Sample wt. gm.	0.1N KBrO_3 cc's.	Pentose found Factor=0.007505 gm.	Recovery per cent.
Arabinose	0.2016	25.50	0.1914	94.9
	0.2005	25.75	0.1943	96.8
	0.2020	25.35	0.1903	94.2
	0.2045	26.00	0.1951	95.4
			Average	95.3
Xylose	0.2038	26.00	0.1951	95.7
	0.2022	25.75	0.1943	96.1
	0.2016	25.80	0.1936	96.0
	0.2009	25.75	0.1943	96.7
			Average	96.1

Distillation Method of Jolles. Jolles advised that the pentose sample be placed in a distilling flask with 200 cc. of 12 per cent HCl and steam distilled, boosting at such a rate that the volume decreased to about 100 cc. while the steam from 800 cc. of water was led through it. More 12 per cent HCl was then added, and the process repeated as long as furfural was produced. The temperatures obtained during this type of distillation were always from 103°-104°, which indicated that the acidity of the hydrolysate received in the neighborhood of 12 per cent throughout the distillation. The lack of destruction of furfural observed by Jolles must then be due, either to the low acidity during distillation, or to the prompt removal of the furfural by the current of steam passing through, or both.

To determine which of these factors was the more important, samples of pure pentoses and of the pentosan materials mentioned above were distilled with steam from both 12 and 20 per cent HCl. The heat was adjusted so that temperatures of 103-104° were maintained in the 12 per cent distillation while temperatures of 107-108° were held in the 20 per cent distillations. Within the limits of experimental error, theoretical results were in all cases obtained from the pentoses used regardless of the concentration of acid used. This is shown in Table III. The pentosan materials gave constant yields indicating that no loss of furfural had occurred, (see Table IV). Furthermore, the rate of distillation did not affect the yield as shown by the marked differences in volumes of distillates obtained.

TABLE III

Pentose Distillations by Steam from 12 and 20 per cent HCl Solutions.

HCl con.	Materials.	Sample wt. gm.	Vol. Dist. CC's.	O.1N. KBrO ₃ cc's.	Pentose found Factor=0.007505.	Recovery per cent.
12 o/o	Arabinose	0.2030	715	27.00	0.2026	99.8
	"	0.2020	650	27.00	0.2026	100.3
	"	0.2014	900	26.80	0.2011	99.9
	"	0.2005	1200	26.70	0.2004	99.9
20 o/o	"	0.2030	1250	26.75	0.2008	100.2
	"	0.2040	755	26.75	0.2008	100.2
	"	0.2000	900	26.75	0.2008	100.3
	"	0.2010	1050	26.75	0.2008	99.9
					Average	100.1
12 o/o	Xylose	0.2003	400	26.65	0.2000	99.8
	"	0.2010	620	26.75	0.2008	99.9
	"	0.2040	1000	27.00	0.2026	99.3
	"	0.2020	425	26.85	0.2015	99.7
20 o/o	"	0.2035	300	27.25	0.2045	100.4
	"	0.2045	375	27.25	0.2045	100.0
	"	0.2033	500	27.15	0.2038	100.2
	"	0.2016	825	26.80	0.2011	99.8
					Average	99.9

TABLE IV

Pentosan Distillations by Steam from 12 and 20 per cent HCl Solutions.

Per cent acid by weight.	Sample.	Grams.	Vol. Dist. cc's.	O.1 N. KBrO ₃ cc's.	Pentosan found Factor=0.006605.	Pentosan per cent.
12	Gum Arabic	0.5018	820	24.50	0.1618	32.2
"	" "	0.5033	1160	24.25	0.1602	31.8
"	" "	0.5053	725	24.65	0.1628	32.2
"	" "	0.5016	925	24.40	0.1611	32.1
20	" "	0.5004	640	24.25	0.1602	32.0
"	" "	0.5053	685	24.50	0.1618	32.0
"	" "	0.5047	940	24.50	0.1618	32.1
"	" "	0.5036	900	24.50	0.1618	32.1
					Average	32.1
12	Sawdust	1.0020	935	23.25	0.1535	15.3
"	"	1.0017	875	23.25	0.1535	15.3
"	"	1.0056	1000	23.35	0.1542	15.3
"	"	1.0064	900	23.50	0.1552	15.4
20	"	2.0020	615	46.40	0.3064	15.3
"	"	2.0014	710	46.25	0.3054	15.3
"	"	2.0049	625	46.50	0.3071	15.3
"	"	2.0032	600	46.50	0.3071	15.3
12	"	1.0026	575	23.00	0.1519	15.1 +
"	"	1.0077	870	23.25	0.1535	15.2 +
"	"	1.0018	530	23.25	0.1535	15.3 +
					Average	15.3

+These distillations were carried out according to Heuser's method (1921), the samples being macerated with 4 per cent NaOH before being distilled with acid. No increased yield of pentosan was obtained. Heuser's determinations always ran 4 per cent higher by this treatment. Hence the above data further substantiates the claim that theoretical yields of furfural are obtained from pentosans by the proposed distillation procedure.

Evidently even a slow current of steam is sufficient to sweep out the furfural as fast as it is formed from the pentoses.

A comparison of the pentose results in Tables II and III indicates that the reason low results are obtained by the official method is that some of the furfural is destroyed by long contact with strong acid. Moreover, this destructive effect can be entirely eliminated by carrying a slow current of steam through the hydrolysate thereby removing the furfural as fast as it is produced. Hence the following method for the quantitative production of furfural from pentose materials is proposed.

Proposed Method for the Distillation of Pentoses.

Place a 2-5 gram sample of the material, and 200 cc. of 12 per cent hydrochloric acid (sp.gr. 1.06) in a 750 cc. distilling flask fitted up for steam distillation. Conduct a slow current of steam into the mixture as soon as the latter reaches the boiling temperature heat the distilling flask with a low flame so that the boiling temperature remains between 103-105° as measured by a thermometer inserted in the vapor in the neck of the distilling flask. By observing this precaution the addition of fresh acid will rarely be required. Distillation is continued until a drop of the distillate no longer gives a red coloration with aniline test paper on being allowed to stand 3-5 minutes. By following the above procedure theoretical yields of furfural have been obtained from all of the pure pentose materials which have been tested. Representative data are found in Table V.

TABLE V

Pentose Distillations by the Proposed Method.

Material.	Sample wt. gm.	0.1 N. KBrO ₃ cc's.	Factor gm. pentose. ----- cc. 0.1N KBrO ₃
Arabinose	0.2000	26.50	0.00755
	0.2005	26.50	0.00755
	0.2015	26.75	0.00753
	0.2021	26.85	0.00752
	0.2030	27.00	0.00752
	0.2025	27.00	0.00750
	0.2037	27.25	0.00747
	0.2040	27.25	0.00748
		Average	----- 0.007515
Xylose	0.3020	40.00	0.00755
	0.3035	40.30	0.00753
	0.3010	40.00	0.00752
	0.3027	40.30	0.00751
	0.3040	40.45	0.00754
	0.3070	41.00	0.00749
	0.3082	41.20	0.00749
	0.3044	40.50	0.00752
		Average	----- 0.007519
		Total Average	0.007517
		Theoretical	0.007505

II. THE DETERMINATION OF FURFURAL

HISTORICAL

Many reagents have been proposed for the estimation of the furfural obtained from the acid distillation of pentose. The principal ones are reviewed below.

Ammonia

The earliest method proposed was that of Stone and Tollens (1888) which involved the precipitation of the furfural by ammonia and subsequent weighing of the resulting furfuralamide. The method was quite unsatisfactory due to incomplete precipitation of the furfural (Günther, de Chalmot and Tollens (1891) Stone (1891)).

Phenylhydrazine

This was proposed by the work of Fischer (1884). Günther and Tollens (1890) and Günther, de Chalmot and Tollens (1891), titrated furfural with a standardized phenylhydrazine solution using aniline acetate paper as indicator. Stone (1891) used Fehling's solution to determine the end point. Ling and Nanji (1921) precipitated the furfural and determined the excess phenylhydrazine by iodometry. Flint and Tollens (1892) and others have shown that the use of this reagent in volumetric estimations is rather unsatisfactory due to instability of the solution and the fact that it reacts with levulinic acid arising from hexoses, giving an indefinite end point. Phenylhydrazine was also used as a gravimetric

reagent (de Chalmot and Tollens (1891, 1891a), de Chalmot (1893, 1893a, 1894). Günther, de Chalmot and Tollens (1891), Flint and Tollens (1892) and Mann, Krüger and Tollens (1896) undertook comparative studies of all the phenylhydrazine methods and concluded the gravimetric method was best. However the furfural hydrazone was difficult to dry properly and conversion factors had to be determined experimentally. This reagent has also been used in the gasometric determination of furfural (Gregoire and Carpiaux (1898), Menaul and Dowell (1919)).

Pyrogallol

Hotter (1893) heated acidified furfural solutions with pyrogallol in a sealed tube at 110° and weighed the resulting precipitate.

Semioxamizine

This was used by Kerp and Unger (1897) who obtained low results with its use. Kreeman and Klein (1917) also used it in their study of the kinetics of the reaction whereby pentoses are transformed into furfural.

Phloroglucinol

Wheeler and Tollens (1889, 1889a) first applied phloroglucinol as a color test and Counciler (1894) adapted the test to the gravimetric estimation of furfural. The method was studied by Welbel and Zeisel (1895) Mann, Krüger and Tollens (1896)

Tollens (1902) and Grund (1902). The first of these found that methyl furfural was also precipitated so that methylpentoses could be determined by the same method. (Votocek (1897), Widtsoe and Tollens (1900)). Kröber (1900, 1901) amplified and perfected the whole pentose procedure and determined, by actual experiment, the factors and tables for the conversion of various weights of phloroglucinol precipitate into the corresponding weights of arabinose, xylose, pentose and pentosan. Kröber's results were verified by Kröber, Rimbach and Tollens (1902, 1902a). Mayer and Tollens (1907) then extended the Kröber procedure to include fucose while Ellett and Tollens (1905) did the same for rhamnose. The latter investigators further found that both methylpentoses and pentoses could be estimated in the same sample by applying Votocek's (1897) observation on the relative solubilities of methylfurfural- and furfuralphloroglucide in 95 percent alcohol at 60°C. Ishida and Tollens (1911) advised the use of a Soxhlet apparatus in the alcoholic extraction but Schorger (1917) showed that this is less accurate than simple maceration of the precipitate with alcohol. Schorger further claimed that the procedure of Ellett and Tollens gave results which were too high for both pentose and methylpentose. Pinoff (1905) studied the reaction between furfural and phloroglucinol in alcoholic solution. Böddinger and Tollens (1910) proposed shortening the time required for precipitation by heating the solution but this modification has been criticized (Wichter and Tollens (1911), Schorger (1917)). Welbel and Zeisel (1895)

advised weighing the precipitate in a weighing bottle because they believed it to be oxidized during drying and weighing in air. This contention was supported by Goodwin and Tollens (1904) and by Cunningham and Doree (1914) but denied by Mann, Krüger and Tollens (1896), and Kröber (1900). Kröber (1901) found that on exposure to the air, the precipitate took up moisture which was later removed with difficulty.

The above conflicting evidence prompts the suspicion that the furfural-phloroglucinol precipitate does not have a fixed chemical composition. Various molecular proportions between furfural and phloroglucinol are cited by different writers who further disagree as to the number of water molecules that are eliminated in the reaction. Goodwin and Tollens (1904) claimed that one molecule of water split out at ordinary temperature while at 80° three were lost. Kröber, in compiling his tables and formulae, assumed that two molecules were eliminated. Evidently no one has had the same pure compound for analysis. The latest work is that of Votocek and Potmesil (1916) in which furfural was used to precipitate phloroglucinol from acid solution. These experimenters found, from a large number of determinations, that the ratio of condensation product to phloroglucinol was "about 2 : 1". Goodwin and Tollens and Kröber stated, however, that the variable composition of the precipitate could probably be dis-

regarded without introducing any appreciable error. This is due to the purely empirical nature of the method.

Barbituric Acid Derivatives

The use of this reagent was suggested by Conrad and Reinbach (1901) and developed by Jäger and Unger (1902, 1903). Fromherz (1907) and Dox and Plaisance (1916) criticized the method and the latter investigators also found malonylguanidine to be unsatisfactory. They found, however, that thiobarbituric acid precipitated furfural quantitatively from acid solution as a definite crystalline chemical compound. They also suggested that the proportions of methylfurfural and furfural present could be calculated from the nitrogen and sulfur content of the precipitate. Hydroxy methylfurfural did not interfere.

Sodium Bisulfite.

Jolles (1905) proposed the addition of an excess of standard sodium bisulfite solution to a neutralized aliquot of the distillate and titration of the excess by iodine. He also estimated both pentoses and methylpentoses by precipitating the former as barium pentosate (Bey (1900)) and performing a double distillation (Jolles 1907). The method was studied by Tolman and Trescott (1906) and Kerp and Wöhler (1909), who found that conditions had to be closely duplicated to obtain concordant results.

Fehling's Solution

The reduction of Fehling's Solution by furfural was proposed as a possible method by Flohil (1911) and further studied by Eynon and Lane (1912) and by Baker and Hulton (1916), who found the presence of sodium chloride to be an influencing factor.

Silver Oxide

The oxidation of furfural by ammoniacal silver oxide was used in a volumetric procedure by Cormack (1900) who titrated the excess silver by thiocyanate after filtration of the silver precipitate. Cormack's method has never been applied to the determination of pentoses.

THE PRESENT OFFICIAL METHOD

The method of the Association of Official Agricultural Chemists (1920) is essentially the Kröber modification of the Tollens method. A weighed sample is distilled with 100 cc. of 12 per cent hydrochloric acid at such a rate that 30 cc. pass over in 10 minutes, when another 30 cc. of acid are added and the process repeated until 12 fractions are received. An amount of phloroglucinol, double that of the furfural expected, is then added to the total distillate which is made up to 400 cc. and allowed to stand over night. The amorphous precipitate is filtered off, washed, dried and weighed in a tared Gooch crucible.

After applying a solubility correction, the corresponding weight of pentose or pentosan is calculated using Kröber's factors.

The principal points of criticism of the present method are:-

1.-The method is empirical and is not based on the molecular weight of the condensation product, also solubility corrections are necessary (Dox and Plaisance (1916)).

2.- Theoretical yields of furfural are never obtained.

3.- The actual yields of furfural are conditioned by the rate of distillation and by the concentration of acid (de Chalmot (1893, 1894), Counciler (1894) Welbel and Zeisel (1895), Wenzel and Lazar (1913), Falada, Stein and Ravniker (1914), van Haarst and Olivier (1914), Kreeman and Klein (1917)). The usual yields of furfural obtained are recorded in Table I.(page 4).

4.- The various pentoses all yield different amounts of furfural. Kröber therefore as well as Tollens (1896) had to use a different factor in his calculations for each specific sugar. Hence an unknown material should be examined qualitatively. All the recorded data on the pentosans in wood is unreliable since woods usually contain both araban and xylan (Schorger (1917) Schwalbe (1919)). The presence of certain substances in the sample may prevent the liberation of the furfural (Seilliere (1909)).

5.- Phloroglucinol precipitates substances other than furfural which are frequently present. Hydroxymethylfurfural, produced from hexose materials, is the chief one of these. (Dull

(1895), Kiermayer (1895), Mⁿther and Tollens (1904), van Ekenstein and Blanksma (1910), Jⁿger and Unger (1902), Krⁿber, Rimbach and Tollens (1902). The interference of this substance has been avoided by fermentation of the hexoses (Spoehr(1919) and by re-distilling the distillates (Fraps (1901), Cuninghame and Doree (1914), Oshima and Konds (1918)). The former method is inaccurate due to fermentation of pentoses (Gillet (1917), Cross and Tollens (1912), Pellet (1916)) while in the latter method furfural is destroyed (Fraps (1901), van Haarst and Olivier (1914)). Moreover the fact that hydroxymethylfurfuralphloroglucide is soluble in alcohol casts doubt on the existing methylpentosan data (Cuninghame and Doree (1914). Schorger (1917) further points out that woods have never been proved to contain methylpentosans.

6.- Substances other than pentose may yield furfural in the distillation. Glucuronic acid is the only compound for which this has been proved (Tollens (1909)), although oxycellulose, fats and oils and their decomposition products are said to yield furfural (Bray and Staidl (1922)).

EXPERIMENTAL

In the search for a satisfactory method for the determination of furfural, several procedures were tested out.

Sodium Hypoiodite

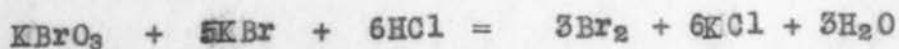
It was at first thought that iodine would be suitable. This reagent reacted with furfural only in alkaline solution. Moreover the amount of iodine taken up was almost a direct function of the alkalinity, if the latter was low, as indicated in Figure 1, while in strongly alkaline solutions concordant results could not be obtained. Although the amount of iodine used up appeared to approach a maximum, the results could not be accurately duplicated.

Acid Permanganate.

Acid permanganate was then tried but soon abandoned because large and indefinite volumes of permanganate were reduced to manganese dioxide by small quantities of furfural.

Potassium Bromate.

At this point the use of potassium bromate was suggested by the work of Okuda (1919) on the oxidation of cystine. This reagent reacts as follows in acidified potassium bromide solution (Treadwell and Hall (1919))



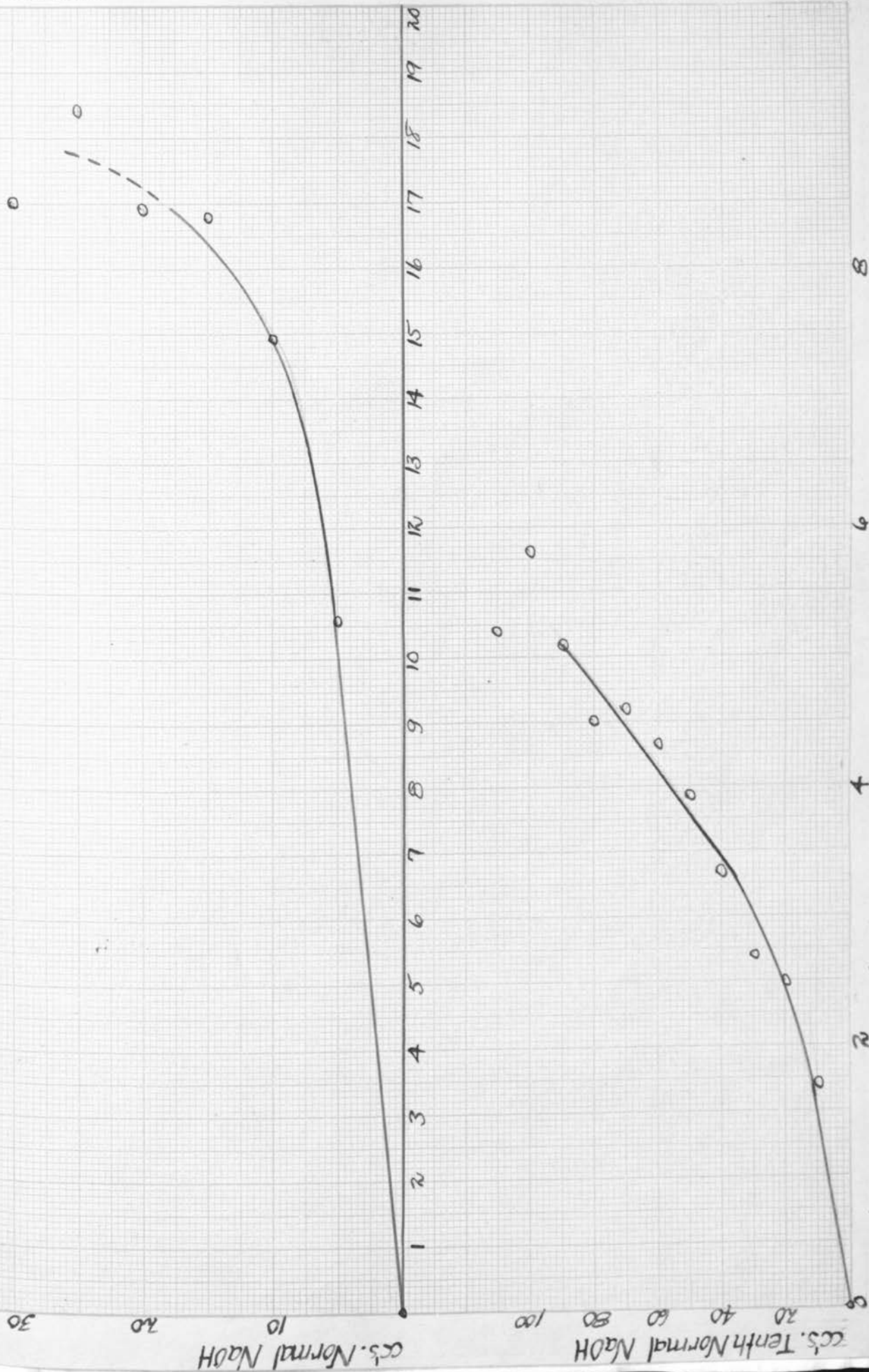


FIG. 1.

cc's Iodine Used up by Furfural

According to Wedekind (1901) furfural can be readily oxidized and brominated in aqueous solution. It was therefore hoped that the reaction between furfural and bromine could be made the basis of a satisfactory method for the determination of furfural, provided an accurate means of finding the end point could be devised. Okuda used the yellow color due to free bromine as indicating the end point. In a preliminary test it was found that this could more accurately be found by the use of a simplified electrometric apparatus. With the use of the latter, a study of the optimum conditions for the titration of furfural by potassium bromate in acidified potassium bromide solution was undertaken.

Materials used

Two specimens of furfural were used, one of which was obtained from Eimer and Amend while the other had been prepared by graduate students working in the department of Chemical Engineering. Both samples distilled at 159°-160° giving pale straw colored distillates. Under reduced pressure, these gave water white distillates which were used in making up the furfural solutions. All of the solutions titrated had been freshly prepared from colorless furfural only a few hours previously. Old furfural solutions usually gave results

which were somewhat in excess of the theory. A weighed quantity was dissolved in distilled water and made up to a definite volume, from which aliquots were withdrawn for analysis.

"Chemically Pure" potassium bromate was used, which, after drying, gave on analysis 99.99 o/o $KBrO_3$. The tenth normal solution requires 2.7837 gm. per liter. The bromate solutions were standardized according to the method recommended by Merck (1914), in which 30-40 cc. are run into an acidified potassium iodide solution and the mixture allowed to stand several minutes, after which it is diluted and the iodine titrated with standard thio-sulfate in the usual manner.

A 20 o/o solution of potassium bromide free from bromate was used.

Apparatus

The apparatus used (see Figure 2) consists of a galvanometer G, key K and two platinum wires, one of which, B, is sealed into the side of a small pipette P and held at a fixed potential by immersion in an acidified solution of 20 o/o KBr containing a trace of free bromine. The other Pt wire C, is immersed in the solution to be titrated in the beaker A. The potential of this wire depends upon the composition of the solution being titrated. A small electric stirrer insures thorough mixing of the unknown solution.

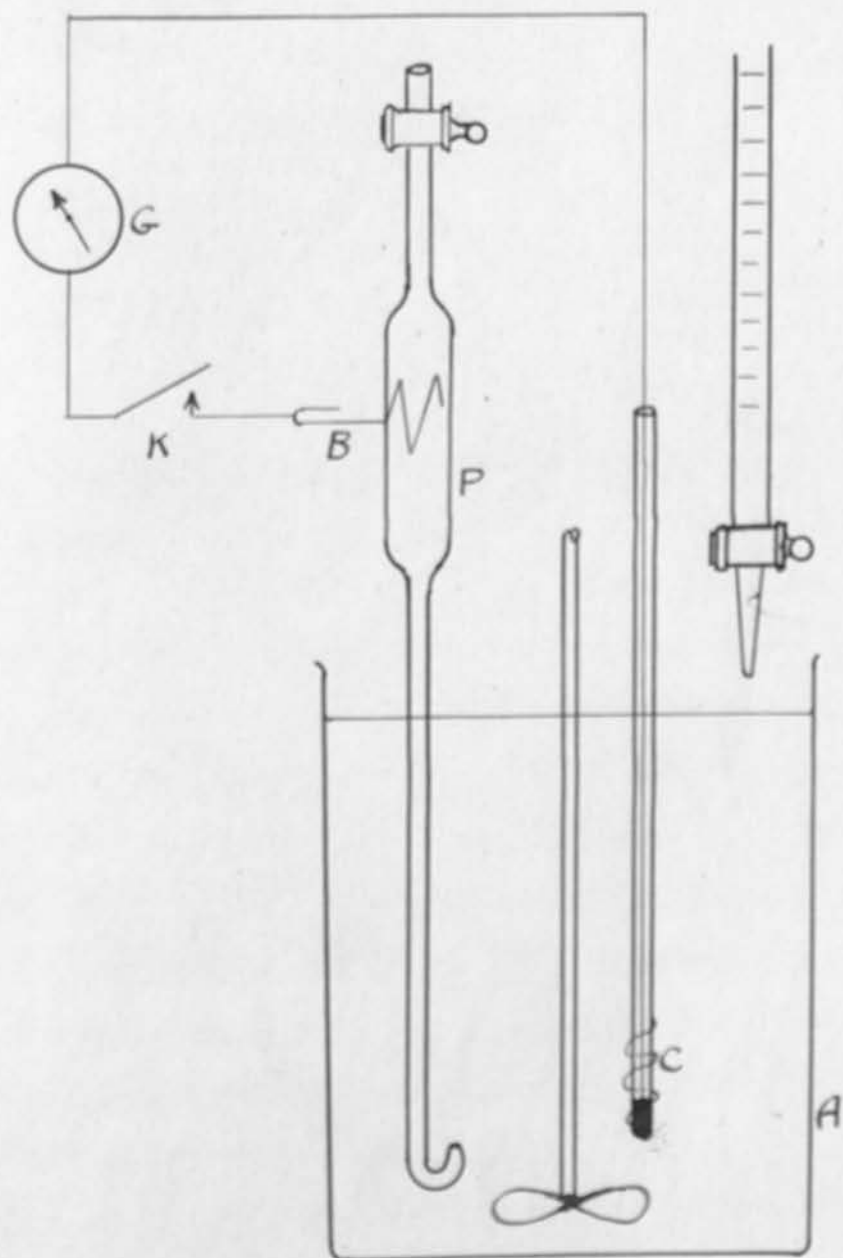


FIG. 2.

Before beginning the titration, depression of the key K will cause the galvanometer to deflect several divisions to the right or left, depending upon the exact manner in which the connections are made, whereas after the titration is completed, the presence of an excess of KBrO_3 in the beaker will cause a throw of the needle in the opposite direction. Obviously, when depression of the key causes no deflection, the potential of both Pt wires is the same and the concentration of free bromine in A is practically equal to that in P. This is the end point.

Method.

In the following preliminary experiments the titrations, were carried out as follows: The bromate solution was added to the furfural solution rather slowly until near the end point, when 3-5 drops were added at a time until the point was found at which, at the end of 2 minutes, a mere trace of free bromine was present as indicated by no deflection of the needle on closing the galvanometer circuit. This was taken as the end point. Since the molecular ratio of furfural to KBrO_3 was unknown equal quantities of furfural were always used so that the burette readings would serve as an index as to the accuracy of the work. The factor for converting the standard bromate solution into furfural was computed later (Table XI). It was used in this place to facilitate comparisons.

Factors Effecting the Titration

Acidity of the solution. The first factor studied was the effect of acidity. To 10 cc. volumes of a furfural solution, 10 cc. of 20 per cent KBr were added and the resulting solution diluted to about 100 cc. Varying amounts of HCl were then added and the furfural titrated with KBrO_3 as already described. After titration of the furfural, 10 cc. of the solution were withdrawn and the acidity determined by titration with standard alkali. The results are shown in Table VI. It is evident that the degree of oxidation of the furfural is a function of the acidity of the solution but at low acidities, (1.4 to 4.3 per cent HCl) the process stops at the first stage and the further action of bromine takes place only slowly. A more accurate study of this last point is discussed later. In the most weakly acid solutions, the reaction appeared to occur rather slowly so that the bromate could only be added drop by drop. When the acidity was 3 to 4 o/o, however, the bromine was liberated promptly and much less time was therefore required for the titration. Moreover, accurate results were easily obtained provided the acidity did not exceed 4 o/o. This acidity was therefore adopted as standard.

Specific acid used.- The substitution of 4 per cent sulfuric acid by weight for hydrochloric acid had no influence on the results as is shown in Table VII.

TABLE VI.

Effect of Acidity on the Titration of Furfural Solutions
 0.1002 gm. furfural used in each case.

HCl per cent.	0.1 N KBrO ₃ cc's.	Furfural found Factor = 0.004803.	Recovery per cent.
1.4	20.70	0.0994	99.2
1.4	20.75	0.0997	99.5
1.4	20.85	0.1001	100.0
1.5	20.70	0.0994	99.2
2.6	20.80	0.0999	99.7
2.6	20.88	0.1003	100.1
2.7	20.85	0.1001	100.0
2.8	20.83	0.1000	99.9
4.0	20.55	0.0987	98.5
4.1	21.00	0.1009	100.7
4.2	20.80	0.0999	99.7
4.3	20.95	0.1006	100.4
5.0	21.00	0.1009	100.7
5.2	22.60	0.1085	108.4
5.2	22.25	0.1069	106.7
5.3	22.15	0.1064	106.2
6.8	24.52	0.1178	117.6
7.0	25.00	0.1201	119.8
7.0	25.40	0.1220	121.8
7.2	24.80	0.1191	118.9

TABLE VII
Effect of Specific Acid Used.

0.1006 gm. furfural used in each case.

Acid used.	Per cent by wt.	0.1 N KBrO ₃ cc's.	Furfural found Factor=0.004806	Recovery per cent.
HCl	3.8	21.00	0.1009	100.3
"	4.0	20.75	0.0997	99.1
"	4.1	21.00	0.1009	100.3
			-----	-----
		Average	0.1005	99.9
H ₂ SO ₄	5.0	20.85	0.1001	99.5
"	4.2	20.85	0.1001	99.5
"	4.5	20.90	0.1004	100.2
"	4.0	20.75	0.0997	99.1
"	3.5	20.90	0.1004	100.2
"	6.0	21.00	0.1009	100.3
"	4.1	21.00	0.1009	100.3
"	4.2	20.80	0.0999	99.2
			-----	-----
		Average	0.1003	99.8

Concentration of KBr. The second factor studied was the influence of the concentration of potassium bromide on the results. Solutions containing 0.1002 gm. of furfural, 10 cc. of 20 per cent KBr and 3 to 4 per cent of HCl in total volumes varying from 100 to 1000 cc. were titrated with bromate. The results appear in Table VIII. It is apparent that the concentration of KBr does not consistently affect the titration. The irregular results are due to the fact that, at the time these determinations were made, the end point had not been carefully studied. A concentration of 2 per cent KBr was used in all subsequent determinations.

Concentration of furfural. In Table IX are brought together the results of trials in which the concentration of furfural was varied while that of both HCl and KBr was maintained constant. It was concluded from these results that, within the limits studied, the concentration does not affect the accuracy of the titration.

Rate of addition of bromate. In Table X are recorded some results in which the bromate solution was added rapidly until the end point was nearly reached. After all the bromine had disappeared the titrations were finished in the usual way. However, the results ran too high, showing that it was necessary to add the reagent slowly, avoiding the presence of any large excess of free bromine, if accurate results were to be expected. In all subsequent work, therefore, the bromate was added slowly enough so that the solutions were never more than faintly yellow colored at any time.

TABLE VIII.

Effect of Concentration of KBr Present

0.1002 gm. furfural used in each case.

KBr per cent.	0.1 N KBrO ₃ cc's.	Furfural found gm.	Recovery per cent.
2.0	20.80	0.0990	99.7
1.0	20.75	0.0997	99.5
0.7	20.70	0.0994	99.2
0.5	20.90	0.1004	100.2
0.4	21.10	0.1013	101.2
0.4	21.40	0.1028	102.6
0.3	20.90	0.1004	100.2
0.3	22.00	0.1057	105.5
0.2	21.05	0.1011	100.9
0.2	21.35	0.1025	102.4
		-----	-----
	Average	0.1012	101.1

TABLE IX.

Effect of Concentration of Furfural

0.1002 gm. furfural used in each case.

Furfural per cent.	0.1 N KBrO ₃ cc's.	Furfural found Factor 0.004803.	Recovery per cent.
0.10	21.10	0.1013	101.2
0.06	20.60	0.0989	98.8
0.05	20.90	0.1004	100.2
0.03	21.10	0.1013	101.2
0.02	21.05	0.1011	100.9
0.01	21.10	0.1013	101.2
0.01	20.95	0.1006	100.4
0.005	21.15	0.1016	101.4
		-----	-----
	Average	0.1008	100.7

TABLE X

Effect of Rate of Addition of Bromate Solution

0.1002 gm. furfural used in each case.

O.1 N. KBrO_3 added rapidly at start. cc.	Final titer O.1 N KBrO_3 cc.	Furfural found Factor=0.004803. gm.	Recovery. per cent.
18.00	21.20	0.1018	101.6
19.00	21.45	0.1030	102.8
20.50	21.75	0.1045	104.3
		-----	-----
	Average	0.1031	102.9
	O.1 N KBrO_3 added slowly from start cc's.		
	20.70	0.0994	99.2
	20.75	0.0997	99.5
	21.00	0.1009	100.6
		-----	-----
	Average	0.1000	99.8

The end point. Having established the proper acidity and concentration of bromide required for the titration, the next problem was to improve the technique so that more concordent results might be obtained.

Towards the end of the reaction between furfural and bromine, the oxidation is quite slow so that the oxidation potential of the solution is never constant. Therefore the potentiometric method of determining the end point was not found suitable. It was then decided to determine the end point by using the time factor itself in connection with the same simple set-up shown in Figure 2.

For this purpose solutions of known furfural content were titrated to within 2 or 3 cc. of the end point, when the addition of the bromate solution was continued in 0.25 cc. increments. The time required for each increment to interact was observed by the use of the galvanometer and a watch. As soon as the deflection fell to zero the next increment of bromate was added and the process repeated until the end point had been crossed. The time required for disappearance of the bromine was then plotted against the total volume of $KBrO_3$ that had been added. Several characteristic curves are shown in Figure 3. The shape of these curves indicates that there are two possible reactions between furfural and bromine, but that one of these is far more rapid than the other in the presence of 4 o/o acid. This causes the curves to rise almost perpendicularly after the principal reaction has been completed.

The selection of the end point from such curves is rather

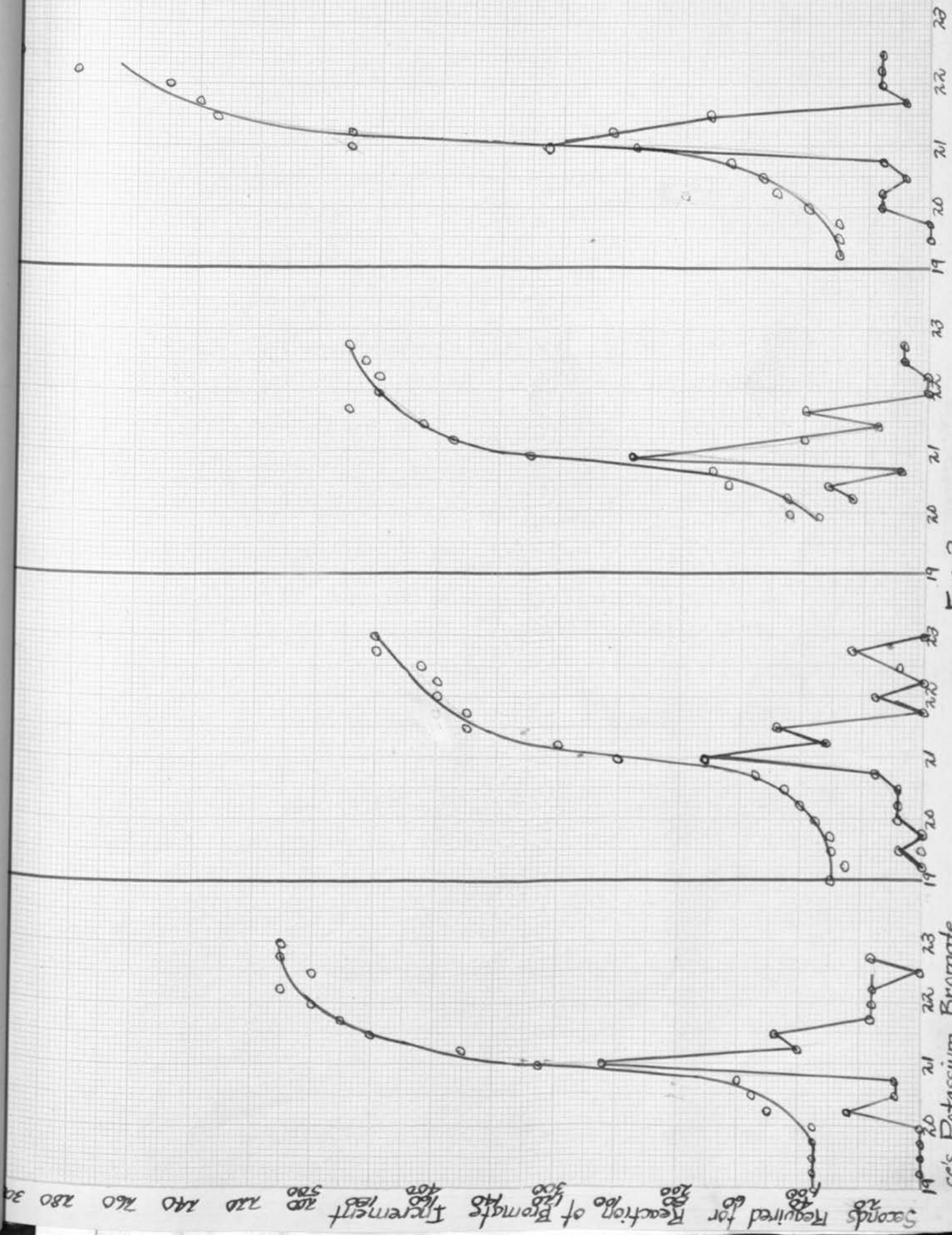


FIG. 3.

cc's. Potassium Bromate.

difficult. If, however, the value $\frac{dt}{dv}$, where dv is the increment of bromate added and dt is the increase in time required for its disappearance over that required by the preceding increment, is plotted against the total volume of bromate used, a curve is obtained which passes through a maximum at the end point. This is best shown by the specific example given in Figure 4. The lower set curves in Figure 3 shows the advantage of the method of plotting the results. Each upper and lower curve was plotted from the same data.

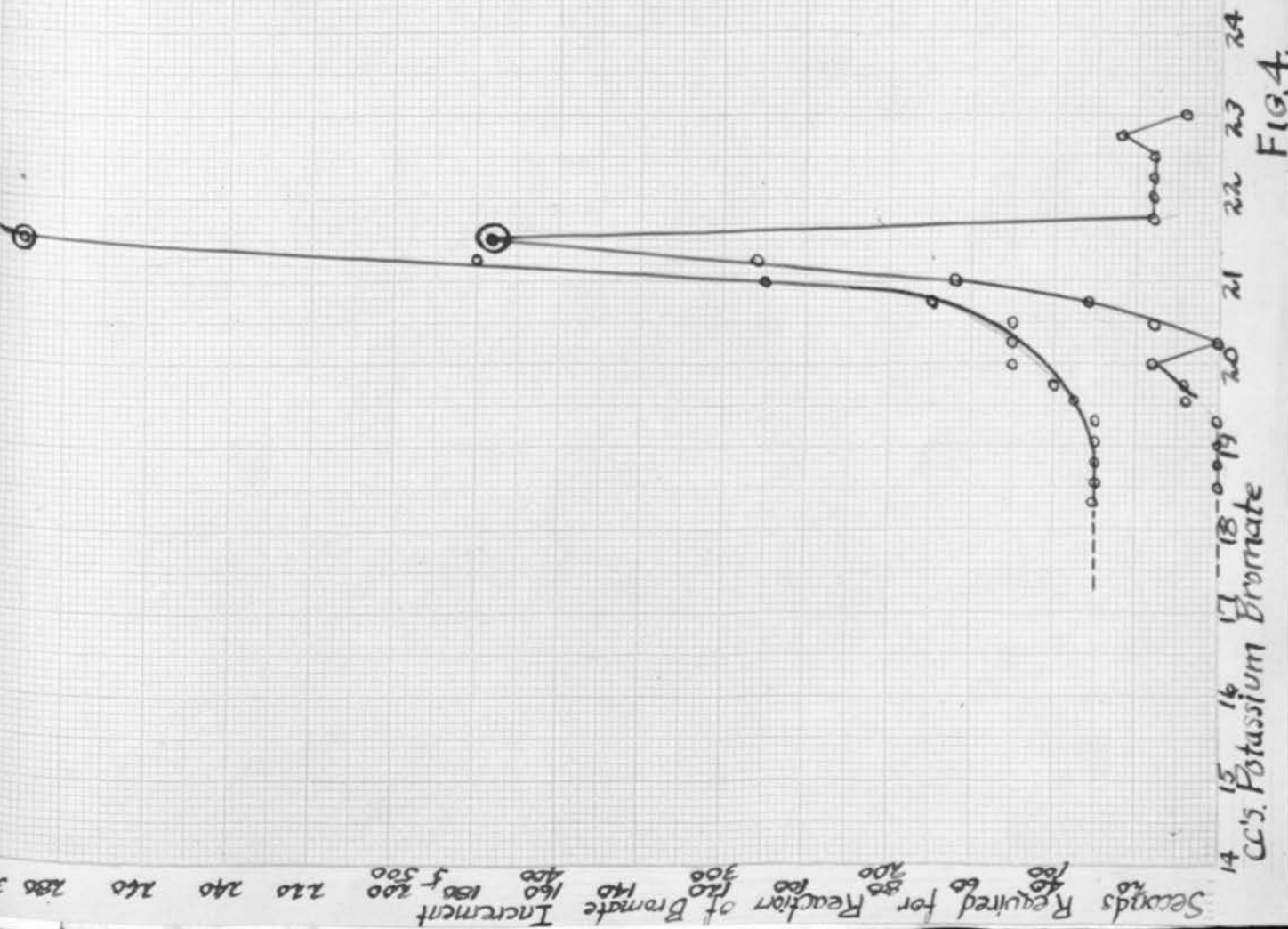
Thus the end point of the titration is obtained by measuring the time required for 0.25 cc. increments of bromate to react and plotting $\frac{dt}{dv}$ against the total volume. The abscissa corresponding to the point of maximum inflection of the curve is the true end point.

The results of a series of determinations on known solutions of colorless furfural run according to the above procedure are recorded in Table XI. Since this procedure appeared eminently satisfactory, the factor for converting bromate to furfural was calculated from the results.

A comparison of the results in Tables VI to X with those in Table XI shows much greater concordance in the latter. This suggests that the cause of error when an arbitrary 2 minute end point was used, was probably the effect of small variations in acidity of the solution. However, such variations apparently affect both the reactions between furfural and bromine to nearly the same extent so that when the results

0.1N HBrO ₃ cc's	time sec.	dt sec.	dy cc's	dt/dy
18.30	30	-	-	-
18.55	30	0	0.25	0
19.00	30	0	0.25	0
19.05	30	0	0.25	0
19.30	30	0	0.25	0
19.55	35	5	0.25	20
19.75	40	5	0.20	20
20.00	50	10	0.25	40
20.25	50	0	0.25	0
20.50	50	0	0.25	40
20.75	70	20	0.25	80
21.00	110	40	0.25	160
21.25	180	70	0.25	280
21.50	290	110	0.25	440
21.75	300	10	0.25	40
22.00	310	10	0.25	40
22.25	320	10	0.25	40
22.50	330	10	0.25	40
22.75	345	15	0.25	60
23.00	350	5	0.25	20

0.1N HBrO₃ reqd. = 21.50 cc
 Furfural found = 0.1033 gm.
 Recovery % = 100.3 %



14 15 16 17 18 19 20 21 22 23 24
 cc's. Potassium Bromate
 FIG. 4.

TABLE XI

Analyses of Furfural by the Proposed Method.

Furfural used gm.	0.1N KBrO ₃ cc's.	Factor gm. pentose/cc. 0.1 N KBrO ₃	Furfural found Factor=0.004803 gm.	Recovery per cent.
0.1007	21.00+	0.00480	0.1009	100.1
0.1007	21.00+	0.00480	0.1009	100.1
0.1007	20.90+	0.00482	0.1004	99.7
0.1007	21.10+	0.00477	0.1013	100.6
0.1007	21.05	0.00478	0.1010	100.3
0.1007	20.85	0.00483	0.1001	99.4
0.1007	20.95	0.00481	0.1006	99.9
0.2014	42.00	0.00480	0.2017	100.1
0.2014	42.00	0.00480	0.2017	100.1
0.2014	41.95	0.00480	0.2014	100.0
0.2014	42.05	0.00479	0.2018	100.2
0.2014	42.05	0.00479	0.2018	100.2
0.1030	21.40	0.00481	0.1027	99.7
0.1030	21.50	0.00479	0.1032	100.2
0.1030	21.60	0.00477	0.1037	100.6
0.1030	21.50	0.00479	0.1032	100.2
0.1030	21.50	0.00479	0.1032	100.2
0.1030	21.50	0.00479	0.1032	100.2
0.2060	43.25	0.00476	0.2076	100.8
0.2060	43.00	0.00479	0.2064	100.2
0.2060	43.25	0.00476	0.2076	100.8
0.2060	43.00	0.00479	0.2064	100.2
		-----		-----
Average		0.004792		100.2
Theoretical		0.004803		100.0

† The curves for these results appear in Figure 3.

are plotted the end point is still readily located.

To verify this statement a final set of experiments were carried out in which the acidities were varied. The results are shown in Table XII and plotted in Figure 5. The intensifying effect of the acid is clearly apparent from the slope of the upper set of curves. Nevertheless the end points were readily found by replotting the data in the manner advised above.

Conversion factor for furfural. The factors in Table XI were obtained by dividing the number of cc's. of 0.1N $KBrO_3$ used by the corresponding weight of furfural. A close agreement is apparent, the average being 0.004792. Moreover the theoretical ratio, based on a molecular ratio of potassium bromate to furfural of 1:3, is 0.004803 from which the experimental factor differs by less than 0.3 per cent. This is well within the limits of experimental error of the method so that the use of the theoretical factor for the purpose of calculation is justified. Theoretical factors were used throughout in the present studies, a procedure which is impossible in the present official method for determining furfural and pentoses.

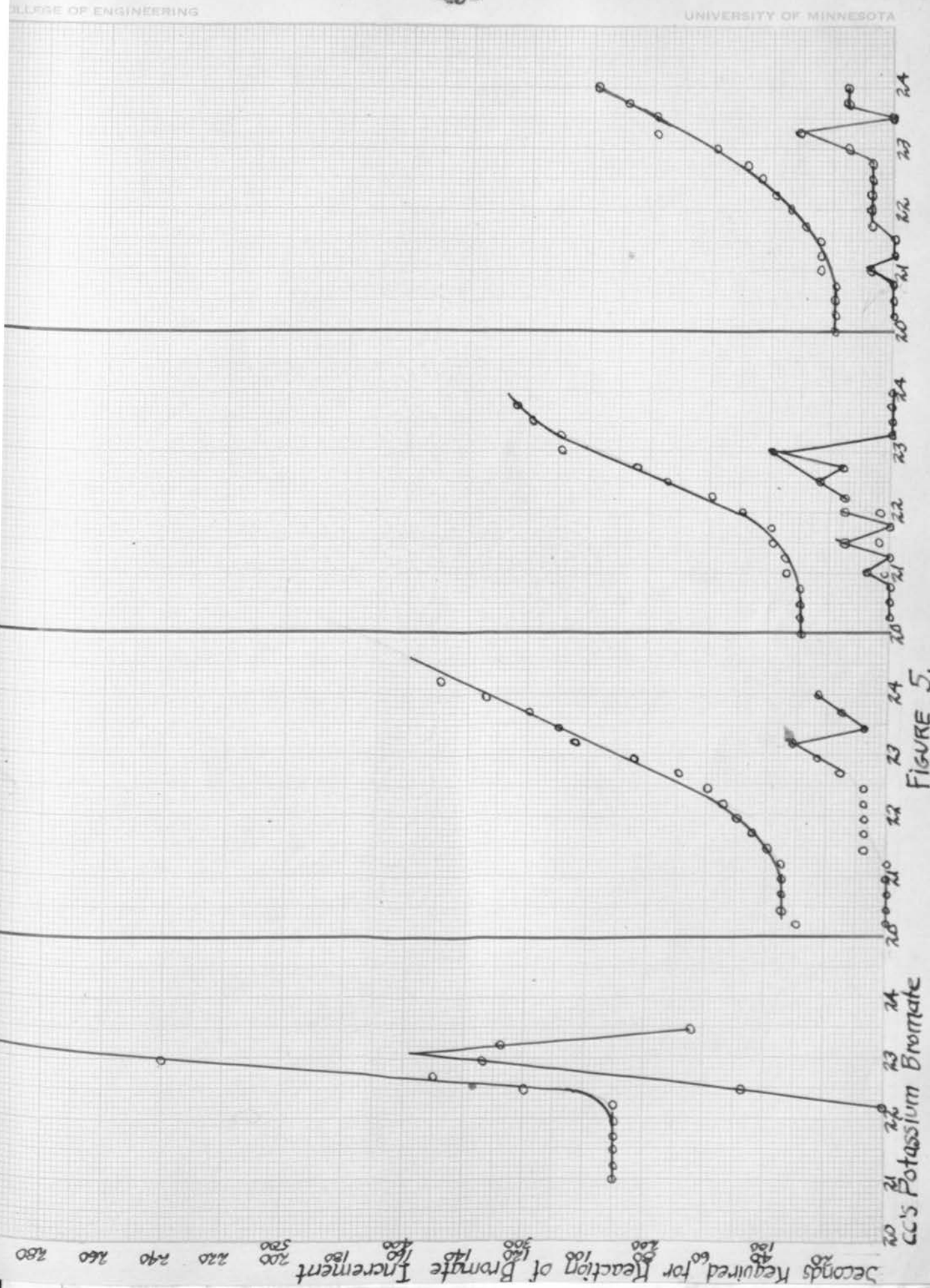
The effect of interfering substances on the proposed method. Furfural distillates from pentose containing materials always contain levulinic acid and hydroxymethylfurfural when hexose materials are present. Therefore a study of the possible effect of these substances was undertaken.

TABLE XII.

Analyses of Furfural by the Proposed Method in
Solutions of Varying Acidities.

0.1112 gm. furfural used in each case.

HCl by wt. per cent.	0.1N KBrO ₃ cc's.	Furfural found gram.	Recovery per cent.
1.8	23.15	0.1112	100.0
4.0	23.15	0.1112	100.0
5.0	23.00	0.1105	99.3
6.1	23.25	0.1117	100.4
	Average	----- 0.1111	----- 99.9



CC's Potassium Bromate

FIGURE 5.

The effect of levulinic acid. Five determinations were run on furfural solutions containing varying amounts of Kahlbaum's levulinic acid. The results are recorded in Table XIII. It is evident that the presence of this substance had no influence on the results in the cases tried.

The effect of hydroxymethylfurfural. Since no supply of this substance was available, weighed samples of glucose, sucrose, lactose and starch were distilled by the method adopted for pentoses and the distillates titrated. The results are shown in Table XIV. As a further check, the determinations shown in Table XV were made, using mixtures of equal quantities of pentose and hexose. It is apparent from the results cited that hydroxymethylfurfural has a slight effect on the titration of furfural, but that this is small enough to be disregarded in many instances since the error thereby introduced is small.

From a study of the above results the following method for the determination of furfural in aqueous solutions is suggested:

Proposed Method for the Determination of Furfural.

To the solution containing 0.1 to 0.2 gm. furfural, 10 cc. of 20 per cent KBr are added for every 100 cc. of solution, and the acidity adjusted to about 4 per cent by weight by adding either acid or alkali as required. With continual stirring, tenth normal KBrO_3 solution is then run in from a burette at such a rate that the

TABLE XIII

Effect of Levulinic Acid

0.2016 gm. furfural used in each case. Total volume before titration 100 cc.

Levulinic acid Added gms.	0.1 N KBrO ₃ cc.	Furfural Found Factor=0.004803.	Recovery per cent.
0.3	41.90	0.2012	99.8
1.	42.05	0.2020	100.2
2.	42.00	0.2017	100.1
3.	41.80	0.2008	99.6
5.	42.00	0.2017	100.1
		-----	-----
	Average	0.2015	100.0
0	42.00	0.2017	100.1
0	41.80	0.2008	99.6
0.	42.15	0.2024	100.4
0	42.00	0.2017	100.1
		-----	-----
	Average	0.2016	100.0

TABLE XIV

Effect of Hydroxymethylfurfural

2.0 gm. samples used in each case.

Material used.	0.1 N KBrO ₃ cc's.	"Furfural" found Factor=0.004803 gm.	"Furfural" per cent.	"Pentose" Factor=0.007505 per cent.
Glucose	1.00	0.0048	0.24	0.38
"	0.50	0.0024	0.12	0.18
Sucrose	1.00	0.0048	0.24	0.38
"	0.75	0.0036	0.18	0.28
Lactose	1.00	0.0048	0.24	0.38
"	1.00	0.0048	0.24	0.38
Starch	0.75	0.0036	0.18	0.28
"	0.75	0.0036	0.18	0.28
			-----	-----
			Average 0.20	0.32

TABLE XV

Effect of Hexoses on the Determination of Pentoses

0.3 gm. each of xylose and sucrose used in each case.

0.1 N KBrO ₃ cc's.	Pentose found Factor=0.007505 gms.	Recovery per cent.
39.90	0.2994	99.8
40.10	0.3010	100.3
40.10	0.3010	100.3
40.25	0.3021	100.7
40.35	0.3028	100.9
40.40	0.3032	101.1
40.50	0.3040	101.3
40.50	0.3040	101.3
	Average	----- 100.7

production of a distinct yellow color throughout the solution is avoided. When the end point is approached a pale yellow color will be apparent immediately after the addition of a few drops of bromate solution, but this soon fades. When this point is reached, the bromate is added in 0.2 to 0.3 cc. increments and the time is recorded which is required for the disappearance of free bromine as indicated by the use of a galvanometer set-up as already explained (See Figure 2). As the end point is crossed, a rather large increase in the time required will be noted. The observations should be carried slightly beyond this point. Finally, the ratio of increment of time to increment of standard KBrO_3 is plotted against the total volume of KBrO_3 already used, and the end point found from the curve thus obtained. The number of cc's. of 0.1 N. KBrO_3 required multiplied by 0.004803, gives the grams of furfural in the sample.

SUMMARY

A study was made of the factors influencing the production of furfural from pure arabinose, pure xylose, gum arabic and pine sawdust. The data presented seem to warrant the following conclusions:-

1.- Distillations of pentose materials, carried out according to the method of the Association of Official Agricultural Chemists, take place from hydrochloric acid of 18 to 20 per cent instead of from 12 per cent acid as usually stated.

2.- Hydrochloric acid of this concentration has a considerable destructive effect on furfural, and is no doubt partly responsible for the low yields of furfural that are obtained from all pentoses when the official method is used.

3.- The passage of a slow current of steam through the distillation mixture is sufficient to carry the furfural off as rapidly as it is formed, thereby avoiding the destruction of furfural by long contact with strong acid.

4.- A method for distilling pentoses from acid solution by steam is described, in which theoretical yields of furfural are always obtained.

Several new volumetric methods for the determination of furfural in dilute aqueous solution were tested out. Iodine in alkaline solution could not be used because the results could not be accurately duplicated. The trials with acid permanganate were also

unsuccessful due to catalytic reduction of the permanganate by furfural. The use of potassium bromate in acidified furfural solutions containing potassium bromide was eminently successful.

The studies concerning the potassium bromate method led to the following conclusions:

- 1.- The acidity of the solution to be titrated should not exceed 4 or 5 per cent by weight; because
- 2.- Further oxidation of the primary product of the interaction of bromine and furfural results in the presence of high concentrations of acid.
- 3.- The velocity of this secondary reaction under the conditions proposed, appears to be so small as to be without appreciable effect on the titration.
- 4.- Either hydrochloric or sulfuric acids may be used.
- 5.- An approximate concentration of 2 per cent potassium bromide is satisfactory.
- 6.- The potassium bromate solution must be added slowly avoiding the presence of any considerable excess at all times.
- 7.- The amount of furfural present does not influence the accuracy of the method.
- 8.- In titrating dilute solutions with potassium bromate, the end point can be readily located by the use of a simplified electrometric apparatus consisting of two platinum wires, a galvanometer and key.

9.- The time factor of the reaction involved is made the basis of the above method for finding the end point.

10.- Hydroxymethylfurfural, a product of the acid distillation of hexose materials, apparently interferes slightly with the use of the proposed method. However the effect is small enough to be disregarded.

11.- Levulinic acid, a further decomposition product of hexoses, is without any effect whatsoever.

Specific directions are given for obtaining theoretical yields of furfural from pentose materials and for the volumetric determination of this substance in the resulting distillates. Representative results of determinations on pure pentoses and pure furfural are recorded which seem to justify the use of the following theoretical factors for the conversion of potassium bromate used to furfural, pentose or pentosan:

Factors for Converting grams of $KBrO_3$ used.

Required grams.	Method of Calculation.	Factor.	Log.
Furfural	$\frac{3C_5H_4O_2}{KBrO_3}$	1.7254	0.236890
Pentose	$\frac{3C_5H_{10}O_5}{KBrO_3}$	2.6961	0.430736
Pentosan	$\frac{3C_5H_8O_4}{KBrO_3}$	2.3726	0.375225

Factors for Converting cc's. of 0.1N KBrO₃ used.

Required grams.	Method of Calculation.	Factor.	Log.
Furfural	0.0027837 x Factor.	0.004803	$\bar{3}.681513$
Pentose	0.0027837 x Factor.	0.007505	$\bar{3}.875351$
Pentosan	0.0027837 x Factor.	0.006605	$\bar{3}.819873$

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