

150 cc. of water (e. g., on Monday night). The next morning the blocks to be glued are heated in an air bath to 60° C. for 2 hrs. Meanwhile the glue is warmed in a water bath and sufficient water added to make 300 g. of glue and water. When the 2 hrs. have nearly expired the 40 per cent glue solution is warmed in a water bath to 60° C., melted, and thoroughly stirred. Hot water should be at hand to add to the water bath for heating the glue in order that its temperature may be kept at 60° C.

SIZING—The hot blocks are taken from the air bath two at a time; the ends are dipped in hot water and rubbed together. This is repeated until the blocks are thoroughly moist, when they are dipped in the solution, the ends rubbed together, and set aside to dry in the air of the laboratory for 2 days. Sized joints are found to be stronger than unsized.

GLUING—The sized blocks are again heated to

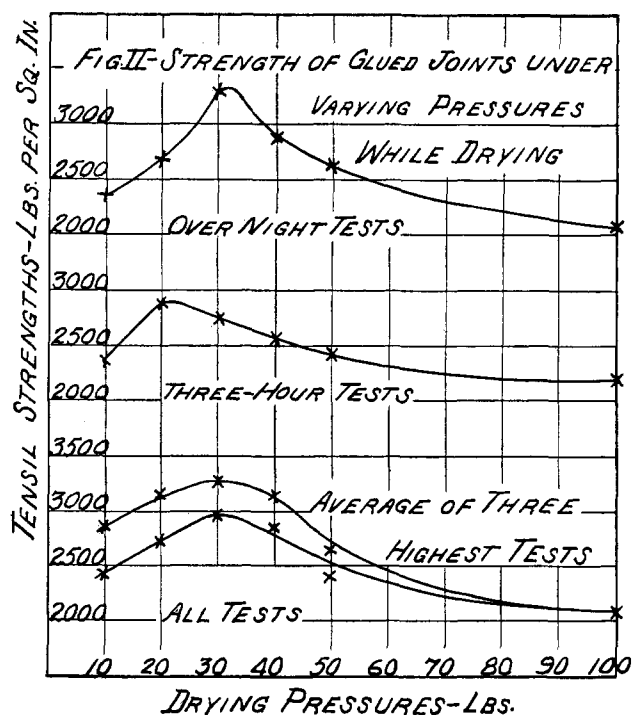


FIG. II

60° C., and the hot 40 per cent glue solution prepared as above. This should be close to the frame where the blocks are to be dried under weights. The blocks are taken from the air bath in pairs and the ends dipped in glue until there is a fairly thick layer on each block. They are then placed together by *sliding* the end of one across that of the other in order to avoid entangling air bubbles, and with due regard to the grain of the wood. The excess of glue around the joint is removed with a penknife. The blocks are placed in the V-shaped frames to secure alignment, put into the rack, and a weight of 30 lbs. per sq. in. is applied before the glue has a chance to peel or dry. Thus one block is glued before the next is taken from the air bath. The blocks are allowed to stay under pressure for 24 hrs., when they are removed, laid on their sides and dried in the air of the laboratory for at least 100 hrs. before breaking.

The results upon some of the preceding glues were as given in Table IX in lbs. per square inch.

TABLE IX—COMPARISON OF RESULTS BY VARIOUS WORKERS

GLUE No. 2 Bone-glue	Esten	Whittlesey			Esten	GLUE No. 5 (Bone-glue) Red-Whit- field tlesey
		field	(a)	(b)		
Average of all.....	2443	2792	3056	2358	3888	1696 2730
Av. of 3 highest.....	1982	2721	3630	3902	3206	5026 1928 2095 3562
Highest.....	2011	5025	3704	4000	3440	5920 1993 3067 3880
Lowest.....	1782	1399	1840	2040	1020	2140 1775 1308 1760

(a) Dec., 1912. (b) Dec., 1913. (c) Glued in April and broken 6 mos. later.

SUMMARY

The preceding work seems to justify the following conclusions:

I—That the tensile strength, jelly test and viscosity of glue bear no relation to each other.

II—That the method followed for tensile strength may be expected to give results with a variation of 10 per cent.

III—That the method of testing the strength of glue by measuring the strength which it imparts to bibulous paper is dependable and gives fairly concordant results.

CHEMICAL DEPARTMENT
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A COMPARISON OF VARIOUS MODIFICATIONS OF THE KJELDAHL METHOD WITH THE DUMAS METHOD OF DETERMINING NITROGEN IN COAL, WITH NOTES ON ERRORS IN THE DUMAS METHOD DUE TO NITROGEN EVOLVED FROM THE COPPER OXIDE¹

By ARNO C. FIELDNER AND CARL A. TAYLOR

The experiments described in this paper were undertaken to ascertain which modifications of the Kjeldahl method are best adapted to the determination of nitrogen in coal, and to check the results if possible with the Dumas gas-volumetric method. The latter method, although difficult and tedious to operate, is generally regarded as fundamental and applicable to almost all classes of organic compounds.

A series of determinations, using some of the best known of the various modifications of the Kjeldahl method, was made on the following eight coals chosen to represent various types and to range in nitrogen from 0.8 to 1.8 per cent:

COAL No.	TABLE I—DESCRIPTION OF COALS		CLASS
	LOCALITY	BED	
1	Morton Co., N. D.....	Lignite
2	Musselshell Co., Mont.....	Sub-bituminous
3	Bureau Co., Ill.....	No. 3	Bituminous
4	New River field, W. Va....	Sewell	Semi-bituminous
5	McDowell Co., W. Va....	Pocahontas No. 3	Semi-bituminous
6	Allegheny Co., Md.....	Davis 6-ft.	Semi-bituminous
7	Fayette Co., W. Va.....	Sewell	Semi-bituminous
8	Campbell Co., Tenn.....	Rex	Bituminous

GENERAL PROCEDURE

A considerable quantity of each sample was prepared by pulverizing the air-dried coal in a porcelain ball-mill to 60 mesh and finer; in fact, most of the material would pass through a 100 mesh sieve.

The general procedure in all of the Kjeldahl methods was essentially as follows: A 1 gram sample was digested in a 550 cc. Kjeldahl flask with 30 cc. concen-

¹ Presented at the Spring Meeting of the American Chemical Society, Cincinnati, April 7-10, 1914, by permission of the Director of the Bureau of Mines.

trated sulfuric acid and the other reagents required in that particular modification. The flask was first heated over a low flame till frothing subsided and then at a temperature sufficient to cause gentle ebullition. The digestions were continued for definite periods of time—2, 3, 4, and 7 hours in the various series. In those cases where potassium permanganate was used, it was added in the form of powder or small crystals, about 10 minutes after turning out the flame. The mixture had then cooled enough to avoid the violent local action that takes place on adding permanganate to the boiling mixture. Adding permanganate under these conditions several times during digestion did not cause appreciable loss of nitrogen, which confirms the results obtained by Siegfried and Weidenhaupt.¹ After cooling and diluting the solution to 250 cc., a few grams of granulated zinc and an excess of sodium hydroxide solution containing potassium sulfide were added and the flask at once connected to a block-tin condenser. To avoid mechanical carrying over of alkali the distillation was conducted very slowly, at the rate of 150 cc. in 1½ to 2 hours. The ammonia was collected in standard sulfuric acid solution and titrated with a standard ammonia solution using cochineal indicator. The solutions were carefully standardized by several methods. Blank determinations were made in all cases, using 1 g. of pure sucrose in place of the coal sample.

EXPERIMENTAL RESULTS

SERIES 1: KJELDAHL METHOD—Table II and the curves in Fig. 1 show the results obtained by digesting the samples

TABLE II—SERIES 1: KJELDAHL METHOD
Digestion with 0.7 g. Hg and 30 cc. H₂SO₄

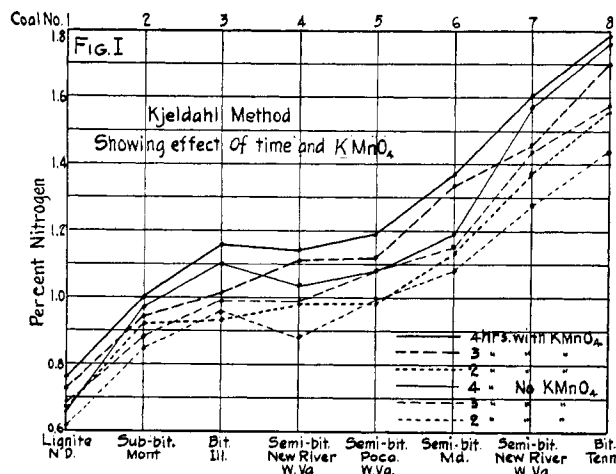
Coal No.	No KMnO ₄ added at end of digestion			KMnO ₄ added at end of digestion			No. hrs. digested before liquid became colorless
	2 hrs.	3 hrs.	4 hrs.	2 hrs.	3 hrs.	4 hrs.	
1	0.63	0.68	0.65	0.65	0.70	0.75	1¾
	0.60	0.68	0.63	0.66	0.75	0.75	
Av.,	0.61	0.68	0.65	0.66	0.73	0.75	
2	0.83	0.89	0.98	0.91	1.01	1.01	2
	0.85	0.88	0.97	0.93	0.93	1.01	
Av.,	0.84	0.88	0.97	0.92	0.94	1.01	
3	0.93	1.03	1.13	0.95	1.02	1.16	2
	1.00	0.95	1.08	0.90	1.04	1.15	
Av.,	0.96	0.99	1.10	0.93	1.02	1.16	
4	0.91	1.01	1.04	0.99	1.10	1.15	1¾
	0.89	0.98	1.04	0.98	1.16	1.13	
Av.,	0.88	0.99	1.04	0.98	1.12	1.14	
5	0.98	1.10	1.10	1.00	1.10	1.18	2
	1.00	1.05	1.08	0.95	1.15	1.20	
Av.,	0.99	1.08	1.09	0.98	1.13	1.19	
6	1.09	1.19	1.21	1.16	1.35	1.36	2¼
	1.08	1.13	1.18	1.08	1.36	1.38	
Av.,	1.08	1.15	1.19	1.13	1.34	1.37	
7	1.26	1.45	1.55	1.39	1.48	1.58	2
	1.29	1.43	1.60	1.36	1.45	1.63	
Av.,	1.28	1.44	1.58	1.37	1.46	1.60	
8	1.40	1.53	1.75	1.56	1.75	1.79	2¼
	1.47	1.58	1.78	1.54	1.67	1.78	
Av.,	1.44	1.58	1.76	1.56	1.70	1.78	

with 30 cc. concentrated sulfuric acid and 0.7 g. of mercury for periods of 2, 3, and 4 hours, both with and without the addition of permanganate after completing the digestion. An in-

¹ Siegfried, Max., and Weidenhaupt, O., "Kjeldahl Nitrogen Determination," *Z. physiol. Chem.*, **76** (1912), 238.

spection of the plotted results shows clearly that the amount of nitrogen obtained increases with the time of digestion and with the addition of permanganate. Apparently this method requires more than 4 hours' digestion to secure the maximum yield of nitrogen.

SERIES 2: KJELDAHL-GUNNING METHOD—Table III and the curves in Fig. 2 show the results obtained by digesting the samples with 30 cc. concentrated sulfuric acid, 0.7 g. of mercury, and 7 g. of potassium sulfate for periods of 2, 3, 4, and 7 hours with and without the addition of permanganate at the end of digestion.



The addition of potassium sulfate to the sulfuric acid and mercury accelerated the rate of oxidation of the coal, the digestion mixture becoming colorless approximately ½ hour sooner than

TABLE III—SERIES 2: KJELDAHL-GUNNING METHOD
Digestion with 0.7 g. Hg and 30 cc. H₂SO₄

Coal No.	No KMnO ₄ added			KMnO ₄ added at end of digestion				No. hrs. digested before liquid became clear
	Per cent N after digesting			Per cent N after digesting				
	2 hrs.	3 hrs.	4 hrs.	2 hrs.	3 hrs.	4 hrs.	7 hrs.	
1	0.61	0.66	0.71	0.68	0.78	0.80	0.80	1¼
	0.64	0.69	0.76	0.71	0.77	0.76	0.78	
Av.,	0.63	0.68	0.74	0.70	0.75	0.77	0.79	
2	0.91	1.05	1.05	0.99	1.05	1.07	1.05	1½
	0.91	1.03	1.04	1.03	1.04	1.05	1.07	
Av.,	0.91	1.04	1.04	1.01	1.04	1.06	1.06	
3	1.12	1.12	1.13	0.98	1.15	1.15	1.18	1¾
	1.10	1.10	1.15	1.07	1.13	1.15	1.16	
Av.,	1.11	1.11	1.14	1.03	1.13	1.15	1.17	
4	1.08	1.19	1.19	1.15	1.16	1.18	1.15	1½
	1.06	1.16	1.19	1.14	1.22	1.20	1.16	
Av.,	1.07	1.16	1.19	1.14	1.20	1.19	1.16	
5	1.19	1.29	1.31	1.26	1.31	1.31	1.20	1¾
	1.23	1.31	1.30	1.21	1.31	1.31	1.33	
Av.,	1.21	1.30	1.31	1.24	1.31	1.31	1.27	
6	1.28	1.33	1.40	1.33	1.36	1.38	1.35	1¾
	1.32	1.33	1.38	1.32	1.38	1.40	1.36	
Av.,	1.28	1.33	1.38	1.33	1.38	1.38	1.36	
7	1.29	1.33	1.39	1.33	1.37	1.39	1.36	1½
	1.62	1.67	1.73	1.57	1.72	1.77	1.66	
Av.,	1.57	1.66	1.74	1.53	1.72	1.76	1.67	
8	1.85	1.83	1.86	1.75	1.76	1.83	1.87	1½
	1.80	1.85	1.84	1.75	1.84	1.85	1.86	
Av.,	1.83	1.84	1.85	1.76	1.82	1.83	1.87(a)	

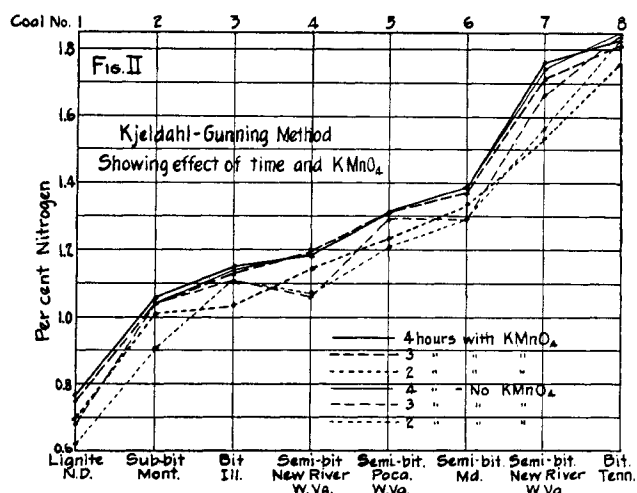
(a) Coal No. 8 digested in the same set for 4 hours gave 1.86, 1.88 and 1.86 per cent N.

In those cases where permanganate was used at the end of the digestion, practically identical results were obtained in the 3-, 4-, and 7-hour periods. The same results were obtained on digesting 4 hours without adding permanganate

at the end; however, on digesting 3 hours without permanganate several low yields were obtained. Hence, adding permanganates according to the method previously described in this paper proved a positive aid to complete oxidation in those cases where the time of digestion was not quite sufficient. In no cases did the addition of permanganate seem to cause any loss of nitrogen.

The greater efficiency of the Kjeldahl-Gunning method as compared with the Kjeldahl method is graphically shown in Fig. 3 which gives a comparison of the nitrogen yields obtained by the two methods on digesting 2, 3, and 4 hours.

SERIES 3: EFFECT OF VARIOUS CONCENTRATIONS OF POTASSIUM SULFATE—Self¹ and Carpiaux² have recently called attention to the danger of volatilization of ammonia during digestion when the composition of the residue approximates that of acid potassium sulfate (KHSO_4). Losses of this nature were avoided by using a large excess of sulfuric acid, *i. e.*, 30 cc. acid to 7 g.



of potassium sulfate. As shown in the results of Table IV, no appreciable diminution in the yield of nitrogen occurred on in-

TABLE IV—SERIES 3: EFFECT OF VARYING AMOUNTS OF K_2SO_4 IN KJELDAHL-GUNNING METHOD

30 cc. H_2SO_4 , 0.7 g. Hg, K_2SO_4 as shown, and KMnO_4 at end of digestion

Coal No.	3 hours digestion			4 hours digestion	
	7 g. K_2SO_4	10 g. K_2SO_4	15 g. K_2SO_4	22 g. K_2SO_4	
1.....	0.77	0.79	0.79
2.....	1.04	1.04	1.05
3.....	1.13	1.14	1.14
4.....	1.20	1.18	1.15
5.....	1.31	1.31	1.32	1.21(a)	1.19
6.....	1.37	1.40	1.40
7.....	1.72	1.72	1.72	1.66(a)	1.68 1.68
8.....	1.82	1.82	1.82	1.76	..

(a) Coal No. 5 digested in the same set, with 7 g. K_2SO_4 gave 1.32 per cent N; coal No. 7 digested in the same set, with 7 g. K_2SO_4 gave 1.72 per cent N.

creasing the potassium sulfate to 15 g. On digesting 4 hours with 22 g. potassium sulfate, losses of from 0.04 to 0.13 per cent nitrogen took place. Apparently the ratio of grams potassium sulfate to cubic centimeters sulfuric acid should not exceed 0.5.

SERIES 4: MODIFICATION FOR NITRIC NITROGEN; KJELDAHL-GUNNING-JODLBAUER METHOD—Table V and Fig. 4 give the results obtained by digesting the coal with 30 cc. sulfuric acid, 7 g. potassium sulfate, 0.7 g. mercury, 2 g. zinc dust, and 2 g. salicylic acid, according to the Jodlbauer modification for nitric nitrogen. The time of digestion was necessarily longer on account of the slow and gradual heating required by this method. The results on digesting 4 $\frac{1}{2}$ hours were approximately the same, within the experimental error, as obtained in the standard

¹ Self, P. A. W., "An Unrecognized Source of Error in the Kjeldahl-Gunning Method for the Determination of Nitrogen," *Pharm. Jour.*, **88** (1912), 384-5.

² Carpiaux, Em., "A Source of Error in the Kjeldahl-Gunning Process," *Bull. Soc. Chim. Belg.*, **27** (1913), 13-14.

Kjeldahl-Gunning method,¹ as anticipated, the samples showed no nitric nitrogen.

TABLE V—SERIES 4: KJELDAHL-GUNNING-JODLBAUER METHOD
30 cc. H_2SO_4 , 7 g. K_2SO_4 , 0.7 g. Hg, 2 g. zinc dust, and 2 g. salicylic acid
All determinations became colorless after digesting 2 hours

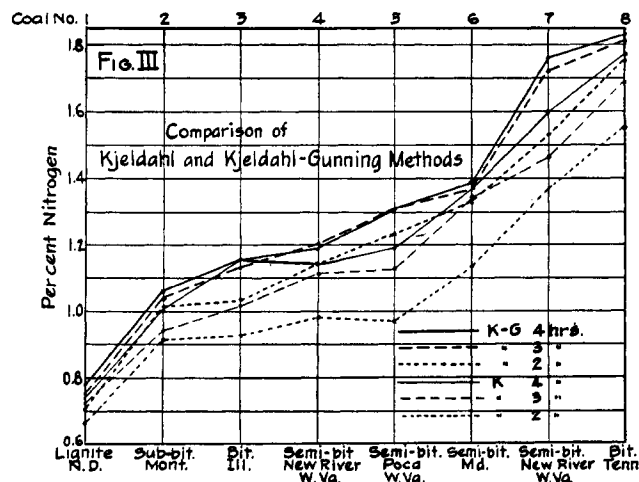
Coal No.	Per cent N after heating			Per cent N by standard Kjeldahl-Gunning method	Difference
	3 hrs.	4 hrs.	4.5 hrs.		
1.....	0.75	0.75	0.78
Av.....	0.78	0.75	0.78	0.77	+0.01
2.....	0.94	0.98	0.98
Av.....	0.93	0.98	0.98	1.06	-0.08
3.....	1.12	1.15	1.17
Av.....	1.07	1.12	1.17	1.15	+0.02
4.....	1.18	1.25	1.20
Av.....	1.25	1.23	1.18	1.19	0.00
5.....	1.24	1.34	1.37
Av.....	1.27	1.39	1.34	1.31	+0.04
6.....	1.15	1.28	1.30
Av.....	1.15	1.25	1.33	1.39	-0.08
7.....	1.62	1.74	1.77
Av.....	1.64	1.74	1.75	1.76	0.00
8.....	1.63	1.74	1.76
Av.....	1.60	1.75	1.80
Av.....	1.65	1.80	1.82	1.83	-0.02
Av.....	1.62	1.77	1.81

SERIES 5: GUNNING METHOD—Table VI and Fig. 4 show the results obtained by digesting the coal 4 hours with 30 cc. sulfuric acid and 7 g. potassium sulfate, according to the Gunning method, and adding potassium permanganate at the end of di-

TABLE VI—SERIES 5: GUNNING METHOD
30 cc. H_2SO_4 , 7 g. K_2SO_4 ; KMnO_4 added at end of digestion

Coal No.	Per cent N after digesting 4 hrs.		Per cent N by standard Kjeldahl-Gunning method	Difference
	Duplicates	Av.		
1.....	0.65	0.65	0.77	-0.12
2.....	0.78	0.75	1.06	-0.30
3.....	0.88	0.93	1.15	-0.25
4.....	0.90	0.95	1.19	-0.26
5.....	1.03	1.00	1.31	-0.30
6.....	1.10	1.15	1.39	-0.26
7.....	1.25	1.20	1.76	-0.53
8.....	1.55	1.48	1.63	-0.32

gestion. This mixture oxidized the coal very slowly; from 3 to 4 hours of digestion were required before the solutions became colorless. All the results were low.



SERIES 6: COPPER-SULFATE MODIFICATION—Table VII and Fig. 4 show the results obtained by digesting coal 3 hours with 30 cc. sulfuric acid, 7 g. potassium sulfate, 1 g. copper sulfate, and adding potassium permanganate at the end of digestion.

¹ Results by standard Kjeldahl-Gunning method refer to the average percentages of nitrogen obtained for each coal in Series 2, digesting 4 hours with 30 cc. concentrated H_2SO_4 , 0.7 g. Hg, 7 g. K_2SO_4 , and adding KMnO_4 at the end of the digestion.

The copper sulfate proved a less effective catalytic agent than mercury, about 45 minutes more time being required to attain a colorless solution. The percentages of nitrogen obtained on digesting 3 hours were from 0.02 to 0.37 per cent less than by the use of mercury. Longer periods of digestion would probably have given the full yield of nitrogen.

TABLE VII—SERIES 6: COPPER-SULFATE MODIFICATION
30 cc. H₂SO₄, 7 g. K₂SO₄, 1 g. CuSO₄, adding KMnO₄ at end of digestion

Coal No.	Per cent N after digesting 3 hrs.		Per cent N by standard Kjeldahl-Gunning method	Difference	
	Duplicates	Av.			
1.....	0.69	0.68	0.68	0.77	—0.09
2.....	1.02	0.99	1.00	1.06	—0.06
3.....	1.04	0.97	1.00	1.15	—0.15
4.....	1.10	1.08	1.09	1.19	—0.10
5.....	1.24	1.27	1.25	1.31	—0.06
6.....	1.22	1.22	1.22	1.39	—0.17
7.....	1.69	1.72	1.70	1.76	—0.06
8.....	1.50	1.53	1.51	1.83	—0.32

SERIES 7: WILFARTH'S MODIFICATION USING P₂O₅—Table VIII and Fig. 4 show the results obtained by digesting the samples 3 hours with 30 cc. sulfuric acid, 6 g. phosphorus pentoxide,

TABLE VIII—SERIES 7: WILFARTH'S MODIFICATION, USING P₂O₅
Using 30 cc. H₂SO₄, 6 g. P₂O₅, 0.7 g. Hg, with KMnO₄ at end

Coal No.	Per cent N after digesting 3 hrs.		Per cent N by standard Kjeldahl-Gunning method	Difference	
	Duplicates	Av.			
1.....	0.73	0.71	0.72	0.77	—0.05
2.....	1.01	0.98	0.99	1.06	—0.07
3.....	1.11	1.06	1.08	1.15	—0.07
4.....	1.13	1.16	1.14	1.19	—0.05
5.....	1.28	1.33	1.31	1.31	0.00
6.....	1.33	1.28	1.31	1.39	—0.08
7.....	1.68	1.73	1.71	1.76	—0.05
8.....	1.63	1.63	1.63	1.83	—0.20

0.7 g. mercury, and adding potassium permanganate at the end of digestion, according to one of the Wilfarth modifications of the Kjeldahl method.

Using the above proportions of reagents, the phosphorus pentoxide was slightly less effective than potassium sulfate, and, furthermore, it is a less convenient material to use.

SERIES 8: DUMAS METHOD—The Dumas gas volumetric method of determining nitrogen is generally regarded as fundamental and applicable to most classes of organic compounds. So, in making an investigation of various modifications of the Kjeldahl method of determining nitrogen in coal, it seemed desirable to check the results by this method.

PROCEDURE—In general, the procedure followed was that given by Gattermann¹ and H. Meyer,² using an open tube and generating pure CO₂ by K₂CO₃ solution and dilute H₂SO₄.⁴ The combustion tube was of fused silica and the nitrogen was collected in a Schiff nitrometer and transferred, for measurement over water, to a water-jacketed gas burette. The tube was charged in the usual manner with a roll of reduced copper gauze 8 cm. long, about 40 cm. coarse CuO, followed by 50 g. fine CuO mixed with the sample. In filling the silica tube, it was found more satisfactory to pour the fine CuO around a glass rod, then remove the rod holding the tube horizontally, thereby leaving a channel across the fine material, than to open the channel by tapping the tube as this tended to form a canal over the coarse oxide also. The fine oxide was reoxidized by heating in the air in an iron dish after each determination. The coarse oxide was so treated as often as it showed any appreciable signs of reduction.

TESTING THE METHOD—To test the method a blank determination was made, using 1 g. of the pure sucrose which is supplied by

¹ Gattermann-Schober, "Practical Methods of Organic Chemistry," p. 85.

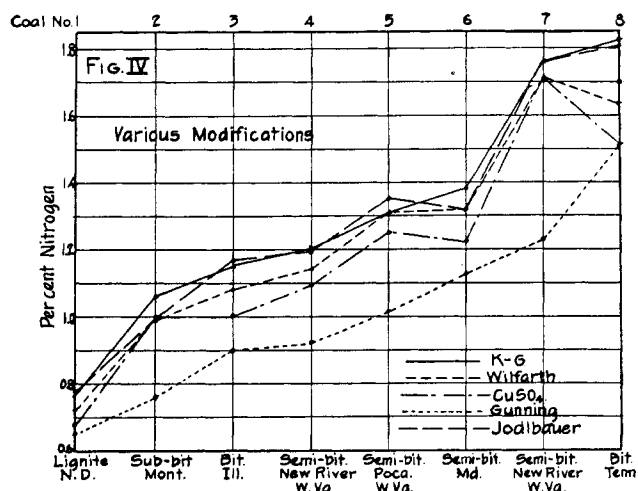
² Meyer, H., "Analyse und Konstitutionsermittlung organische Verbindungen," 2 Auflage, Julius Springer, Berlin, 1909, S. 185.

³ Blau, Fritz, "Verfahren zur Bestimmung des Stickstoffes in organischen Substanzen," M. 13 (1892), S. 277.

⁴ Young, G., and Caudwell, B., "An Improved Apparatus for Generating CO₂," *J. Soc. Chem. Ind.*, 26 (1907), 184.

the Bureau of Standards for calorimeter standardization. There was little difficulty in clearing the cold tube of air so that the CO₂ was completely absorbed. However, on heating the copper oxide and especially that portion of the tube containing the fine oxide and sucrose, fine bubbles of a non-absorbable gas began to collect in the nitrometer. At the end of 2 hours' heating 2 cc. of gas had collected and after 4 hours there were over 4 cc. and the gas was coming slowly but steadily. As the sucrose and CO₂ were both free from nitrogen, the CuO was regarded as the probable source of error.

After cooling the furnace, the CuO was removed and ignited in the iron dish over a Chaddock burner for several hours. (The Chaddock burner gave a more general heat than the Meker, so that the iron dish was not oxidized sufficiently to scale off iron oxide.) The tube was recharged as before except that no combustible material was used. As before, the tube was cleared of air with little difficulty, but on heating the copper oxide a non-absorbable gas was given off. At the end of 6 hours 6.6 cc. had collected. The tube containing CO₂ was allowed to cool overnight, and again heated 7 hours the next day, yielding an additional 1.4 cc. At the end of the second day the evolution had practically ceased. An analysis of this gas showed 5.41 per cent oxygen, a trace of combustible material, and 94.6 per cent of nitrogen. These experiments were repeated using



several different brands of copper oxide but giving essentially the same results. However, oxidized copper wire seemed better than other forms as it was then easier to clear the tube of air. Repeated evacuation of the cold tube with a Geryk pump and refilling with CO₂ aided in removing the air, but failed to materially reduce the gas obtained on heating.

It appeared that copper oxide prepared by igniting and cooling in the air as usually directed retained air which could not be removed by evacuating the cold tube, and which was slowly but persistently given off on heating in an atmosphere of CO₂.

A review of the literature on this subject disclosed the following references: In speaking of the Dumas method, H. Meyer¹ states: "The chief source of error lies in the impossibility of freeing the fine copper oxide from air, and, therefore, most of the results are too high by 0.1 to 0.2 per cent." Fresenius² states: "The results are generally somewhat too high, viz., by about 0.2 to 0.5 per cent;" and that in a blank experiment with sugar the quantity of unabsorbed gas "should not exceed 1 or 1.5 cc."

Abegg and Auerbach³ state that "black copper oxide has the

¹ Meyer, H., "Analyse und Konstitutionsermittlung organischen Verbindungen," 2 Auflage, Julius Springer, Berlin, 1909, p. 187.

² Fresenius-Cohen, "Quantitative Chemical Analysis," 6th ed., Vol. II, p. 68 (1904).

³ Abegg, B., and Auerbach, Fr., "Handbuch der anorganische Chemie," Vol. 2, p. 604.

power of holding gases such as carbon dioxide, oxygen, nitrogen, carbon monoxide, water vapor, etc. This may be by adsorption, solubility in the amorphous phase, or perhaps by chemical combination."

Morse¹ prepares both coarse and fine copper oxide for use by first heating them for 1½ hours or more at a full-red heat in a combustion tube through which is passed a current of oxygen or air. Without cooling, carbon dioxide is then passed through the tube for an hour or more. The oxide is allowed to cool in CO₂.

Phillips² in describing the Dumas method for the determination of nitrogen in natural gas states that "some difficulty was experienced in expelling air from copper oxide when the apparatus was being prepared for work. In beginning a series of determinations several days were often required for the purpose. The porcelain tube was strongly heated, while a slow stream of carbon dioxide was maintained; the CuO was not considered to be in proper condition until the escaping CO₂ was absorbed without residue. It was found that the CuO when once impregnated with CO₂, while strongly heated, could be reoxidized by air current with little tendency to occlusion of air, but if the copper oxide was allowed to cool in contact with air much time was lost in removing the air by carbon dioxide even when strong heat was applied."

As the preliminary determinations confirmed Phillips' observations in regard to the long time necessary to expel the air from copper oxide by merely heating it in a current of CO₂, it seemed desirable to try to shorten the time by heating the

TABLE IX—EXPERIMENTS SHOWING NITROGEN GIVEN OFF FROM COPPER OXIDE ON HEATING UNDER VARIOUS CONDITIONS
Cc. N at 25° C. and 740 mm. pressure, given off on heating 100 g. copper oxide at approximately 850° C. for a period of 2 hours

Experiment No.	METHOD OF TREATMENT	J. T. Baker's CuO,		
		Baker and Adamson 200 mesh CuO Sample A	40-100 mesh CuO Sample B	"wire form," 40-100 mesh Sample C
1	Copper oxide placed in silica tube, evacuated and replaced with CO ₂ repeatedly until no further nitrogen was evolved. It was then heated for 2 hours.	2.5	2.3	0.9
2	Copper oxide from previous experiment, subjected alternately to vacuum and CO ₂ while heated to 850° C. for several hours, then cooled in CO ₂ , exposed to air 18 hours, and tested as in Experiment 1.	2.2	...	0.7
3	CuO from previous experiment treated as in Experiment 2, except exposed to air only 2 hours.	1.9
4	CuO from preceding experiment cooled in CO ₂ , reduced to metallic Cu, re-oxidized, cooled in air, and treated as in Experiment 1.	3.5	3.9	2.7
5	CuO from preceding experiment treated as in Experiment 1.	0.7
6	CuO from preceding experiment treated as in Experiment 4.	3.2

CuO in a vacuum to prepare it for the analyses. Experiments were made to see the advisability of this procedure and to obtain some data tending to show how the nitrogen is held.

EXPERIMENTAL WORK ON NITROGEN HELD BY CuO

As a basis of comparison the gas volume was reduced in each case to the corresponding volume at 25° C. and 740 mm. pressure, that being about the average temperature and pressure at which the experiments were made.

EXPERIMENT 1a—100 grams of Baker and Adamson's CuO of 100 mesh or finer (86 per cent passed through 200 mesh), followed by a reduced copper spiral for removing oxygen, were placed in the silica tube of a combustion furnace. The tube was connected with a nitrometer, an apparatus for generating pure CO₂, and a Geryk pump. The air was removed by the Geryk pump and replaced by pure CO₂ several times, till there was complete absorption on passing CO₂ through the tube. The CuO was then heated to a full-red heat for 2 hours, giving 2.5 cc. of non-absorbable gas.

EXPERIMENT 2a—Heating of CuO in Experiment 1a was continued several hours, applying vacuum repeatedly and replacing the gas by CO₂ until no further non-absorbable gas was liberated. The CuO was cooled in CO₂, then removed from the tube and let stand overnight in the air. It was then replaced in the tube, the air replaced by CO₂ by use of vacuum until there was complete absorption in KOH solution. After heating the CuO 2 hours 2.2 cc. of gas were collected.

¹ Morse, H. N., "Exercises in Quantitative Chemistry," p. 276.

² Phillips, F. C., "Fluctuation in the Composition of Natural Gas," *Proc. Eng. Soc. Western Pa.*, 14 (1898), 299.

EXPERIMENT 3a—Heating *in vacuo* was continued for several hours, CO₂ was then admitted and the tube allowed to cool. When cool the CuO was exposed to air for 2 hours in an open dish and the experiment repeated as in Experiment 1a, giving 1.9 cc. of non-absorbable gas or nitrogen.

EXPERIMENT 4a—The CuO from Experiment 3a was cooled in CO₂, then removed from the tube, mixed with sucrose, replaced in the tube, and largely reduced to metallic copper by heating. It was then removed from the tube, again oxidized in the air as usual, replaced in the tube, and treated as in Experiment 1a. 3.5 cc. of nitrogen were collected after 2 hours' heating.

EXPERIMENT 1b—A fresh sample of the same brand of copper oxide was taken and treated exactly as in Experiment 1a, giving 2.3 cc. of nitrogen.

EXPERIMENT 4b—The CuO from Experiment 1b was reduced with sucrose and treated exactly as in Experiment 4a, giving 3.9 cc. of nitrogen.

In order to show the effect of the size of CuO on the amount of nitrogen retained, a sample of Baker's CuO in "wire form" was pulverized to pass through a 40 mesh screen and remain on 100 mesh.

EXPERIMENT 1c—Using 100 grams of this CuO and treating exactly as in Experiments 1a and 1b, 0.9 cc. of nitrogen was obtained.

EXPERIMENT 2c—This oxide from Experiment 1c was treated exactly as in Experiment 2a, and gave 0.7 cc. of nitrogen.

EXPERIMENT 4c—The oxide from Experiment 2c was reduced

with sucrose and treated exactly as in Experiments 4a and 4b, and gave 2.7 cc. of nitrogen.

EXPERIMENT 5c—The oxide from Experiment 4c was treated as a fresh sample as in Experiments 1a, 1b and 1c, giving 0.7 cc of nitrogen.

EXPERIMENT 6c—The CuO from Experiment 5c was again reduced with sucrose and further treated as in Experiments 4a, 4b and 4c, and gave 3.2 cc. of nitrogen.

EXPERIMENT 7—60 grams of the 40-100 mesh material that had been reduced and reoxidized in air were tested in a special apparatus of glass and quartz with mercury seals at the joints. The CuO was placed in a quartz tube, which was then completely evacuated with a mercury pump. Heat was applied by an electric furnace and the temperature of the CuO raised to 800° C. Over 150 cc. of gas were collected. This was analyzed, showing 89.60 per cent CO₂, 8.34 per cent air, and 2.06 per cent excess nitrogen. The CuO was then removed from the apparatus and heated in air in the open dish for 3 hours and again tested just as described, giving less than 1 cc. of gas under the combined heat and vacuum. The same CuO after being reduced by sucrose and cooled in CO₂ was again heated in the special apparatus *in vacuo* to about 500° C., when such a large quantity of gas was suddenly evolved that the apparatus was broken and further tests discontinued.

A study of the results of Experiments 1 to 6, inclusive, as shown in Table IX, tends to show that the nitrogen given off on heating CuO *in vacuo* or CO₂ is held by the oxide in two ways:

(1) In some form of chemical combination which takes place on oxidizing reduced copper in air.

(2) By adsorption.

Experiments 4 and 6 show that both coarse and fine copper oxide, when partly reduced and reoxidized in air, retain nitrogen which is not completely removed at room temperature by evacuation and replacement with CO_2 , 2.7 to 3.9 cc. of nitrogen being given off from 100 g. oxide on subsequently heating it 2 hours at 850°C . in an atmosphere of CO_2 .

On the other hand, when the CuO was subjected to alternate vacuum and CO_2 for several hours at 850°C . instead of room temperature, until no further nitrogen was evolved, and was then cooled in CO_2 , exposed to air and again heated as in Experiments 4 and 6, the 40-100 mesh "wire" oxide gave off only 0.7 to 0.9 cc. of nitrogen, while the 200 mesh material gave off 1.9 to 2.2 cc.

It seems, then, that adsorption may account for this residual nitrogen which varies in amount with the fineness of the oxide, and that the larger quantity of nitrogen which is obtained on the first vacuum-and-heat treatment subsequent to reoxidation in air of reduced copper is present in some form of chemical combination. The larger error due to the so-called chemically combined nitrogen can be eliminated from the Dumas method by first preparing the copper oxide which is subsequently mixed with the sample, by heating it *in vacuo* for several hours and cooling it in CO_2 . The smaller, but more persistent error, due to adsorbed nitrogen can be reduced by using as coarse an oxide as possible.

Using 50 g. of the 40-100 mesh CuO and coarse oxidized wire, both prepared as above, the sucrose and picric acid gave the following results under the usual conditions of determining nitrogen:

Sample Gram	TIME OF HEATING, 2 HOURS				Nitrogen Mg	Nitrogen Per cent
	Nitrogen cc.	Temperature $^\circ\text{C}$.	Pressure mm. Hg	Nitrogen cc.		
SUCROSE:						
1.0000	0.4	25	740	0.43	0.04	
1.0000	0.1	26	745	0.11	0.01	
1.0000	0.14	30	744	0.15	0.02	
PICRIC ACID:						
0.2000	34.2	27	745	37.1	18.55	
0.2000	33.7	26	740	36.4	18.18	
0.2000	32.8	20	746	36.8	18.41	
0.2000	33.4	23	746	36.9	18.46	

Since the theoretical nitrogen content of picric acid is 18.34, both of these series show that the error is within the limits of the errors of manipulation for most work. In further corroboration, the explosive chemical laboratory of the Bureau has made many nitrogen determinations on various nitrogen compounds with uniform success, by using these precautions in the preparation of the CuO .

In Table X and Fig. 5 are given the percentages of nitrogen obtained by the Dumas method in the previously described eight samples of coal. The procedure was the same as in the sucrose and picric-acid determinations. The average values by the Dumas method check the Kjeldahl-Gunning values to within the total experimental error of the two methods. The larger

TABLE X—SERIES 8: COMPARISON OF RESULTS BY DUMAS AND BY KJELDAHL-GUNNING METHOD

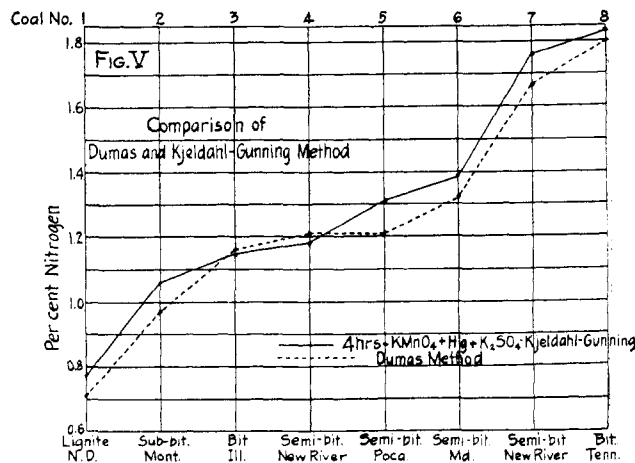
Percentage N by Dumas method				Percentage N by Kjeldahl-Gunning method			
Coal No.	Dumas method	Av.	Diff.	Coal No.	Dumas method	Av.	Diff.
1....	0.73	5.....	1.29
	0.61		1.10
	0.80	0.71	0.77 -0.06		1.23	1.21	1.31 -0.10
2....	1.03	6.....	1.44
	0.90		1.19
	0.97	0.97	1.06 -0.09		1.32	1.32	1.39 -0.07
3....	1.15	7.....	1.61
	1.25		1.65
	1.07	1.16	1.15 +0.01		1.76	1.67	1.76 -0.09
4....	1.21	..	1.19 +0.02	8.....	1.61
					1.86
					1.83
					1.91	1.80	1.83 -0.03

deviations of the individual Dumas values are due to the experimental difficulty in burning a relatively large quantity of carbon as compared to the nitrogen present, without having the nitrogen contaminated with combustible gases, or leaving some

unburned coal in the tube. These sources of error are not common to definite nitrogen compounds.

The volatile hydrocarbons of coal including large amounts of methane are given off readily on heating. These are but slowly oxidized by CuO in the presence of CO_2 ,¹ thereby giving the possibility of too high results.

Furthermore, coal and coke² are oxidized very slowly by CuO in the presence of CO_2 , leaving a possible residue of unburned



carbon even after 2 or 3 hours heating. So without examining the evolved nitrogen for combustible gases and the CuO residue for unburned carbon, there would always be some doubt, in the case of coals, of the accuracy of the individual determinations.

SUMMARY

1—In comparative nitrogen determinations by various modifications of the Kjeldahl method on 7 different coals and 1 lignite, the highest and most concordant results in the shortest time of digestion were obtained by the combined Kjeldahl-Gunning method, using both mercury and potassium sulfate as proposed by Dyer.³ This confirms the results obtained on other organic materials by Sherman and Falk,⁴ Gladding,⁵ Wedemeyer,⁶ Trescot,⁷ and the Committee⁸ on Fertilizer Analysis of the American Chemical Society.

2—When 22 g. of potassium sulfate were used with 30 cc. of acid, no losses occurred between limits of 7 and 15 g. K_2SO_4 per 30 cc. H_2SO_4 .

3—As a catalytic agent mercury proved more effective than copper sulfate, and for raising the boiling point of the mixture, K_2SO_4 was superior to P_2O_5 from every standpoint.

¹ Dunstan and Carr, "Note on a Difficulty in the Determination of Nitrogen by the Absolute Method," *Proc. Chem. Soc.*, **1896**, pp. 48-49.

² Schmitz, G., "Zur bestimmung des Stickstoffes in Steinkohle und Koks," *Z. anal. Chem.*, **25** (1886), 314-318.

³ Dyer, B., "Kjeldahl's Method for the Determination of Nitrogen," *Jour. Chem. Soc.*, **67** (1895), 811-817.

⁴ Sherman, H. C., and Falk, M. J., "The Determination of Nitrogen in Organic Compounds," *J. A. C. S.*, **26** (1904), 1469-74.

⁵ Gladding, T. S., "Comparative Work on Nitrogen Estimation by the Kjeldahl and Gunning Methods and by a Combination of the Two Methods," *Proc. Assoc. Off. Agr. Chem.*, **1906**, 85.

⁶ Wedemeyer, K., "Ein Wort zur Stickstoffbestimmung nach Kjeldahl-Gunning," *Chem. Zeit.*, **22** (1898), 21.

⁷ Trescot, T. C., "Comparison of the Kjeldahl-Gunning-Arnold Method with the Official Kjeldahl and Official Gunning Methods of Determining Nitrogen," *THIS JOURNAL*, **5** (1913), 914.

⁸ "The Determination of Nitrogen in Commercial Ammoniates of High Nitrogen Content," First Report of the Committee on Nitrogen Division of Fertilizer Chemists, *Amer. Chem. Soc.*, *THIS JOURNAL*, **3** (1911), 691.

4—The official Gunning method did not prove applicable to coal as the results on digesting 4 hours were 0.2 to 0.3 per cent low.

5—Modifications for nitrates or nitro compounds did not give results appreciably different from the ordinary Kjeldahl-Gunning method.

6—In no cases could low results be ascribed to the addition of potassium permanganate in the manner described. On the other hand, it seemed to promote higher results in cases of incomplete digestion.

7—In all cases it was found necessary to digest coal approximately 2 hours after becoming colorless, to secure maximum yield of nitrogen.

8—An independent check on the absolute accuracy of the Kjeldahl-Gunning method was obtained by determining the nitrogen in the same samples by the Dumas gas-volumetric method. The greatest difference in the average values was 0.10 per cent and the mean difference was 0.05 per cent.

9—Errors in the Dumas method due to nitrogen from the fine CuO were minimized by previously heating the oxide for several hours *in vacuo*, cooling it in CO₂, and using "wire form" oxide pulverized to pass through a 40 mesh screen and remain on 100 mesh.

The authors desire to acknowledge their obligations to G. A. Hulett, Chief Chemist, for valuable suggestions and criticisms, to G. A. Burrell and his associates for making gas analyses and to G. B. Taylor for making the special vacuum tests of Experiment 7.

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THE DETERMINATION OF GASOLINE VAPOR IN AIR

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In this report are shown results obtained by the Bureau of Mines in determining gasoline vapor in air. One of the methods presented is essentially the same as that used by the authors in determining benzene in artificial illuminating gas¹ except that lower temperatures were used. Briefly stated, this method consists in introducing the gasoline vapor-air mixture into a glass vessel at atmospheric pressure, cooling it by means of liquid air, then withdrawing the air with a vacuum pump, next closing the stopcock on the liquefaction bulb, next removing the liquid air, thereby allowing the gasoline to vaporize and reading its pressure on a manometer attached to the liquefaction bulb.

Dr. G. A. Hulett, Chief Chemist of the Bureau of Mines, first suggested this scheme of analysis to the authors for the determination of water vapor in air. It was a simple matter to apply it to benzene vapor, gasoline vapor, or other vapors in air. The chief requirement is that the vapor be cooled at a temperature where its pressure is practically nil. It was found that the temperature of solid carbon dioxide and acetone (about -78° C.), although low enough to retain benzene (boiling point 80° C.), was not low enough to retain the gasoline the authors worked with. This gasoline had a specific gravity at 15° C. of 0.689 = 73.2° Bé.

¹ Burrell, G. A. and Robertson, I. W. "The Separation of the Illuminants in Mixed Coal and Water Gas," THIS JOURNAL, 7 (1915), 17.

The following fractionation analysis made by Dr. E. W. Dean of the petroleum laboratory of the Bureau shows the fractions obtained at different temperatures: 200 g. of the gasoline were distilled in an unjacketed glass flask at the rate of 2 to 3 drops per sec.

Temperature C.	Percentage by weight	Temperature C.	Percentage by weight
50	0.9	110-120	7.3
50-60	9.0	120-130	4.9
60-70	14.5	130-140	3.2
70-80	14.4	Residue	2.7
80-90	13.8		
90-100	12.9	TOTAL	94.5
100-110	10.9	Loss	5.5

As stated before, experiments by the authors have shown that although benzene (boiling point 80° C.) can be retained at a temperature of -78° C., the gasoline vapor could not. The above fractionation analysis explains why. It will be observed that a considerable portion of the gasoline distilled at temperatures lower than 80° C., hence a temperature that would retain benzene vapor would not necessarily retain the gasoline vapor. Since a temperature lower than that of liquid carbon dioxide had to be used, the authors found it expedient to use the temperature of liquid air, because the latter has to be used, and time is consumed, in obtaining temperatures between those of liquid carbon dioxide and liquid air.

At Fig. 1 is shown the apparatus for the gasoline vapor or benzene-vapor determination. The bulb contains phosphorus pentoxide for removing water vapor. If the latter were not removed it would also be retained at low temperatures and its pressures subsequently measured along with the pressure exerted by the gasoline vapor.

To start a determination the apparatus is connected to a vacuum pump and exhausted of its air. The mixture of gasoline vapor and air is then introduced at atmospheric pressure, the barometer read, and the two bulbs immersed in liquid air contained in a Dewar flask. After waiting about 10 minutes the air is removed from the apparatus with a vacuum pump. The stopcock on the apparatus is then closed, the liquid air removed, the gasoline allowed to vaporize and its pressure read on the mercury manometer attached to the apparatus. The ratio of this pressure to the pressure of the atmosphere gives the percentage of gasoline vapor originally in the air.

The first work of the authors in analyzing gasoline vapor-air mixtures was performed by burning the gasoline vapor with air or oxygen, measuring the contraction in volume and the carbon dioxide produced, and from these data calculating the percentage of gasoline vapor by assuming that it was all pentane vapor. This assumption is wrong because gasoline

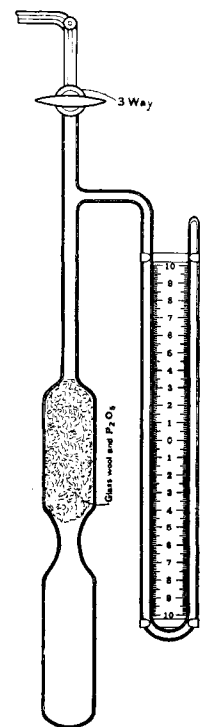


FIG. 1—APPARATUS FOR THE DETERMINATION OF GASOLINE VAPOR IN AIR