sterol from maize oil and from wheat, for the alcohol from olive oil, and for the phytosterol from cottonseed oil.

	Sitosterol.	Alcohol from olive oil.	Phytosterol.
Alcohol	136.5°–138°[1,2,3]	135°–136.5°[4,3]	136°–137°[5]
Acetate	127[1,3]	120.3–120.7[3]	123.5–124[5] 120–121[3]
Propionate	108.5[1,3]	102.5–103.5[3]	104–105[5]
Benzoate	142–145.5[1,2,3]	145–145.5[3]	142–143[5]

While the differences here are less marked than in the case of the olive oil alcohol and cholesterol, the melting-points seem, on the whole, to indicate that the compound from olive oil resembles the phytosterol from cottonseed oil more than sitosterol from maize oil or from cereals, and is undoubtedly phytosterol and not cholesterol.

THE DETERMINATION OF BENZENE IN ILLUMINATING GAS.

By L. M. Dennis and J. G. O'Neill.

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In 1891 Hempel and Dennis described a method[6] for the volumetric determination of certain hydrocarbons that are usually present in illuminating gas. Up to that time, all hydrocarbons in this product, with the exception of methane, had been determined by absorption with fuming sulphuric acid and had been classed under the general term "heavy hydrocarbons." It is true that Bunsen[7] gives an analysis of illuminating gas in which the percentages of benzene, ethylene and propylene are stated, but the amounts of these three gases were calculated by means of equations from the results of explosions with air and oxygen, and the calculation was based upon the assumption that the heavy hydrocarbons in the gas consisted only of ethylene, propylene and benzene. It was ascertained by Hempel and Dennis that certain hydrocarbons such as benzene and naphthalene could be removed, in part at least, by means of absolute alcohol, the remainder of the heavy hydrocarbons being then absorbed by fuming sulphuric acid and the methane being finally determined by explosion or combus-

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[1] Mauthner and Suida: *Monatsh. Chem.*, **15**, 367 (1894).

[2] Ritter: *Ztschr. physiol. Chem.*, **34**, 461.

[3] Gill and Tufts: This Journal, **25**, 254.

[4] Bömer: *Ztschr. Unter. Nahr. u. Genus.* (1898), p. 81.

[5] Bömer and Winter: *Ibid.*, **4**, 864 (1901).

[6] *Ber. d. chem. Ges.*, **24**, 1162.

[7] "Gasometrische Methoden," second edition, (1877), p. 142.

tion. In 1894 Noyes and Blinks adapted[1] the method of Hempel and Dennis to the Bunte burette.

Recent work in this laboratory, however, has shown that while the absorption of benzene by means of alcohol may sometimes give agreeing results, the removal of the benzene is usually by no means complete and the results, at times, show wide variations. The following analyses are given in confirmation of this statement. Air was drawn into a Hempel burette containing water as the confining liquid, and was measured. It was then passed into a gas pipette containing benzene and was drawn back into the burette and the increase in volume noted. The mixture of benzene and air was next passed into a pipette containing mercury and 3 cc. of absolute alcohol, and was shaken for three minutes in contact with the alcohol. The residue was then drawn back into the burette and was passed into a pipette filled with water and was shaken with that liquid for three minutes to remove the vapor of alcohol. The gas was now drawn back into the burette and measured. The results were:

TABLE I.

	I. cc.	II. cc.	III. cc.
Air taken	67.0	50.0	52.2
Air plus benzene (C_6H_6)	73.0	54.0	57.0
After shaking with alcohol	69.0	51.8	54.2
After shaking with water	68.4	51.4	53.7
Benzene taken	6.0	4.0	4.8
Benzene found	4.6	2.6	3.3

Experiments were next tried to ascertain whether repeated treatment with alcohol would remove all of the benzene, and, as will be seen from the table below, it appears that this reagent is unable to remove benzene completely from mixtures of that substance with air.

TABLE II.

				Fresh absolute alcohol.	
	I. cc.	II. cc.	III. cc.	IV. cc.	V. cc.
Air taken	58.6	60.1	63.0	56.8	67.9
Air plus benzene	62.8	64.6	67.0	61.0	72.8
After shaking with alcohol	59.8	61.6	63.8	57.8	69.0
After shaking with water	59.4	61.1	63.8	57.6	68.8
After second shaking with alcohol	59.2			....	...
After second shaking with water	59.1			....	....
After third shaking with alcohol	59.1			....	...
After third shaking with water	59.1			....	....
After passing residue into fuming sulphuric acid and then into the potassium hydroxide pipette	58.7	60.2	62.9	....	....

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[1] This Journal, **16**, 697.

It was therefore apparent from these results that for the complete and speedy removal of benzene from illuminating gas some absorbent other than absolute alcohol must be employed.

In 1897 Hofmann and Küspert described[1] certain compounds of hydrocarbons with metallic salts and stated that when illuminating gas acts upon a mixture of nickel hydroxide and aqua ammonia, there results a compound of nickel cyanide with ammonia and benzene, $Ni(CN)_2.NH_3.C_6H_6$. This statement led the authors of the present paper to examine into the action of an ammoniacal nickel solution upon benzene with the view to ascertaining whether a method could be developed for the volumetric determination of the benzene that is present in the form of vapor in gas mixtures. Sufficient of the absorbent to fill a Hempel simple absorption pipette (about 150 cc.) was prepared by dissolving 25 grams of crystalline nickel nitrate, $Ni(NO_3)_2.6H_2O$, in 50 cc. of water and adding 50 cc. of strong aqua ammonia. The solution was allowed to cool, was decanted from any salt that separated out and strong aqua ammonia was then added until the volume amounted to 150 cc. The solution loses its efficiency if diluted with water, and its absorptive power is greatly diminished if nickel hydroxide is present in suspension. The analytical results given in this paper were obtained with the reagent prepared in this manner. Experiments showed that this solution absorbed nothing from air, but that when shaken with a volume of air it gave off a small amount of ammonia gas. In the first series of experiments it was sought to remove this ammonia by passing the gas mixture into a Hempel pipette filled with water, but, since this did not entirely remove the ammonia, it was found necessary to use in place of the water a 5 per cent. solution of sulphuric acid.

Later experiments made in this laboratory by Mr. W. C. Geer have shown that it is possible to prepare the reagent in such manner as to do away with the necessity of the treatment of the gas mixture with dilute sulphuric acid. The method of preparation of the reagent is as follows: Forty grams of nickel nitrate are dissolved in 160 cc. of water to which has been added 2 cc. of nitric acid of specific gravity 1.44. This solution is poured slowly with constant stirring into 100 cc. of ammonium hydroxide, specific gravity 0.908. The resulting deep blue solution is used in the absorption. It has a very slight tinge of lavender. The odor of

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[1] *Ztschr. anorg. Chem.*, **15**, 204.

ammonia is noticeable, but is not strong. The few analyses that have been made with the reagent prepared in this manner indicate that it is similar in action to that prepared as above described and that it is equally efficient. It should, however, be more thoroughly tested before complete reliance is placed upon it.

In the series of experiments described in the following pages, the analyses were carried out in a "simple" Hempel burette provided with a water jacket, and water was used as the confining liquid.

Experiments were first made to ascertain whether benzene vapor mixed with air can be quantitatively absorbed by the ammoniacal nickel solution just described. The gas mixture was first passed into a pipette containing the ammoniacal nickel solution and was shaken with that reagent for three minutes. It was then drawn back into the burette, passed into a pipette containing mercury. and 5 cc. of 5 per cent. sulphuric acid and was shaken for three minutes, being then drawn back and measured.

TABLE III.

	I. cc.	II. cc.	III. cc.
Air taken	52.7	48.6	51.3
Air plus benzene	56.4	52.4	55.2
After shaking with ammoniacal nickel nitrate solution	53.2	49.0	51.9
After shaking with 5 per cent. sulphuric acid	52.7	48.6	51.3
Benzene taken	3.7	3.8	3.9
Benzene found	3.7	3.8	3.9

The above results show that benzene vapor is quantitatively absorbed by treatment with an ammoniacal nickel solution prepared as above, when the gas mixture is shaken with the reagent for three minutes. Results of approximate accuracy can be obtained by using a simple burette without water jacket, but there seems to be a slight heating of the gas mixture resulting from the absorption of the ammonia gas by the dilute sulphuric acid, this rise in temperature being sufficient to cause appreciable error in the final reading. To ascertain whether the time necessary for the absorption of the benzene could be reduced, other mixtures of benzene and air were prepared and were shaken with the absorbent for one minute, for two minutes, and for three minutes. The results, which need not here be inserted, showed that a three-minute shaking of the gas mixture with the absorbent is necessary for the complete removal of the benzene.

The next point to be ascertained was whether the nickel solution would absorb other constituents of illuminating gas and would so interfere with their determination as to render its use for the absorption of benzene impossible. Measured amounts of carbon dioxide were mixed with measured amounts of air and this mixture was passed into a pipette containing the nickel solution. As was to be expected, the carbon dioxide was completely removed. It had already been found that the nickel solution had no effect upon air, and consequently the absorption of oxygen in the illuminating gas by this reagent did not need further examination. To ascertain whether carbon monoxide and the unabsorbable residue, consisting chiefly of methane, hydrogen and nitrogen, is affected by the nickel solution, the heavy hydrocarbons were removed from 100 cc. of illuminating gas by means of fuming sulphuric acid and potassium hydroxide, and the residue was then shaken for three minutes with the nickel solution and then with the dilute sulphuric acid. No diminution in volume resulted. From these experiments it appears that the ammoniacal nickel solution beyond removing, wholly or in part, the hydrocarbons other than methane, absorbs no other gas except carbon dioxide, but the fact that this last-named gas is removed by the reagent makes it impossible to use the nickel solution for the removal of benzene and allied carbons, and still adhere to the order that is usually followed.[1] In the customary procedure the hydrocarbon vapors are first absorbed by alcohol, then carbon dioxide by caustic potash, and then the so-called heavy hydrocarbons by fuming sulphuric acid. Hempel and Dennis state[2] that carbon dioxide may not first be removed by means of potassium hydroxide because benzene is soluble in that reagent. Experiments were made to ascertain whether this statement is correct. A measured volume of air was mixed with a measured volume of benzene vapor and this mixture was passed over into a pipette containing potassium hydroxide. No diminution in volume resulted. It therefore appears that the absorption of carbon dioxide by potassium hydroxide may properly precede the absorption of benzene. To be perfectly sure upon this point, however, the following experiment was made: Three Muencke wash-bottles containing clear barium hydroxide solution were connected together and illuminating gas was passed through

[1] Hempel-Dennis's "Gas Analysis" (1902), p. 282.

[2] *Ibid.*, p. 281.

this chain. The carbon dioxide present in the gas was completely removed by the reagent in the first bottle. The gas issuing from the third bottle was therefore free from carbon dioxide, but could safely be assumed to contain some of all of the other constituents of illuminating gas. 100 cc. of the gas issuing from the third bottle was drawn off into a Hempel burette and was then passed over into the caustic potash pipette. No decrease in volume took place. A repetition of this experiment gave the same result, and there was thus obtained confirmation of the statement made above, that potassium hydroxide removes nothing from illuminating gas except carbon dioxide.

Experiments were next undertaken to ascertain, if possible, the nature of the hydrocarbons removable by alcohol and by the ammoniacal nickel solution. These hydrocarbons probably consist largely of ethylene, propylene, and benzene. Ethylene was prepared by treating pure ethylene bromide with a zinc-copper couple. The purity of the gas was tested by passing it into fuming sulphuric acid, the confining water in the burette having first been saturated with the ethylene. Ten cc. of the gas left a residue of 0.2 cc., showing a purity of 98 per cent. Measured volumes of air were now mixed with measured volumes of this gas and the mixture was then passed into a pipette containing the nickel solution and then into a pipette containing mercury and 5 cc. of 5 per cent. sulphuric acid. The results obtained were:

TABLE IV.

	I. cc.	II. cc.	III. cc.
Air taken	49.2	51.5	48.0
Air plus ethylene	58.0	60.8	54.2
After shaking with ammoniacal nickel nitrate solution	58.8	62.4	55.1
After shaking with 5 per cent. sulphuric acid	57.9	60.9	54.2

It therefore appearing that ethylene is not taken up by the nickel solution, experiments were next carried out to ascertain whether benzene and ethylene could be separated by means of the nickel solution. The results of these experiments follow:

TABLE V.

	I. cc.	II. cc.	III. cc.	IV. cc.
Air taken	50.2	60.7	48.9	54.4
Air plus benzene	53.0	64.2	51.1	57.2
Air plus benzene plus ethylene	57.6	68.7	57.2	64.4
After shaking with ammoniacal nickel nitrate solution and then with 5 per cent. sulphuric acid	54.7	65.2	54.9	61.6

	I. cc.	II. cc.	III. cc.	IV. cc..
Benzene taken	2.8	3.5	2.2	2.8
Benzene found	2.9	3.5	2.3	2.8
After shaking the residue with absolute alcohol and then with water	53.4	64.6	54.7	61.1
After treatment with fuming sulphuric acid and then with potassium hydroxide	50.7	61.3	49.7	55.3
Ethylene taken (88 per cent. pure)	4.6	4.5	6.1	7.2
Ethylene found by alcohol	1.3	0.6	0.2	0.5
Ethylene found by fuming sulphuric acid and potassium hydroxide after alcohol	2.7	3.3	5.0	5.8
Total ethylene found	4.0	3.9	5.2	6.3
Ethylene taken (corrected volume)	4.04	3.9	5.36	6.3

The results in Table V show that a satisfactory separation of benzene from ethylene and probably from the other hydrocarbons of the ethylene series may be effectd by first shaking the gas mixture with the ammoniacal nickel nitrate solution for three minutes, and then with a 5 per cent. solution of sulphuric acid for the same length of time.

It was hoped that it might be possible to remove the ethylene series of hydrocarbons by means of absolute alcohol before subjecting the illuminating gas to treatment with fuming sulphuric acid. If this were possible, the hydrocarbons would be divided, analytically, into three distinct groups, and a much clearer idea of the illuminants in the gas could then be obtained from the results of a volumetric analysis than is possible under the present methods. The results in Table V have shown that the absorption of ethylene by alcohol is far from complete, and, moreover, that the results of such absorption are by no means constant. It was thought desirable, however, before abandoning the separation by alcohol to try the method with illuminating gas, and in Table VI the results of these experiments are given.

TABLE VI.

	I. cc.	II. cc.	III. cc.	IV. cc.
Carbon dioxide	1.2	1.2	1.1	1.1
Benzene by nickel solution and dilute sulphuric acid	1.2	1.0	1.0	1.0
Hydrocarbons removed by absolute alcohol and water	1.5	0.3	1.3	0.5
Heavy hydrocarbons removed by fuming sulphuric acid and potassium hydroxide	2.3	3.5	2.6	3.4
Total hydrocarbons absorbed by the three reagents	5.0	4.8	4.9	4.9

These results demonstrate conclusively that absorption by alcohol can not be employed for the purpose in hand and that at the present time the gas analyst must content himself with the absorption of benzene by the nickel solution and the subsequent absorption of the so-called heavy hydrocarbons by fuming sulphuric acid. In Table VII are given four analyses of illuminating gas, showing the accuracy of the determinations of carbon dioxide, benzene, and the heavy hydrocarbons.

TABLE VII.

	I. cc.	II. cc.	III. cc.	IV. cc.
Carbon dioxide	1.2	1.2	1.2	1.2
Benzene by nickel solution and dilute sulphuric acid	1.0	1.0	0.9	0.9
Heavy hydrocarbons removed by fuming sulphuric acid and potassium hydroxide	4.0	3.9	3.9	4.0
Total hydrocarbons	5.0	4.9	4.8	4.9

Before the ammoniacal solution of nickel nitrate and the 5 per cent. solution of sulphuric acid are used for the absorption of benzene, the reagents should, of course, be saturated with the other constituents of the gas mixture in the usual manner.[1] If the reagents in the pipettes have been used for analysis of illuminating gas, they should not be used in the examination of generator gas or of any other gas mixture differing appreciably from the illuminating gas, for the gases that have been dissolved by the reagent when it was shaken with the illuminating gas would escape into another superimposed gas mixture, if this latter did not contain these dissolved gases at approximately the same partial pressure as that at which they existed in the gas with which the reagent was first shaken. Consequently the gas pipettes should be filled with fresh solutions of ammoniacal nickel nitrate and sulphuric acid whenever the gas mixture to be analyzed differs markedly from that for which the reagents had previously been used.

The results may briefly be summarized as follows:

(1) Under the described conditions, alcohol does not completely remove either benzene or ethylene from gas mixtures.

(2) The use of an ammoniacal solution of nickel nitrate furnishes a rapid and exact method for the determination of benzene

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[1] Hempel-Dennis's "Methods of Gas Analysis," (1902), p. 119.

in mixtures of that substance with air and ethylene, and in coal gas.

The authors would recommend that in the analysis of illuminating gas (coal gas), the order of procedure be: (*a*) The absorption of carbon dioxide by potassium hydroxide; (*b*) the absorption of benzene by the ammoniacal solution of nickel nitrate above described; (*c*) the absorption of the "heavy hydrocarbons" by fuming sulphuric acid; (*d*) the absorption of oxygen by alkaline pyrogallol or by phosphorus; (*e*) the absorption of carbon monoxide by cuprous chloride; and (*f*) the determination of the methane and hydrogen.

The authors have been unable to try this new method on any commercial gas mixture other than the local supply of illuminating gas. They would therefore earnestly request chemists using the method on other gas mixtures to communicate to them the results of such analyses and call their attention to any difficulties that may arise.

CORNELL UNIVERSITY, ITHACA, N. Y.,
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ON THE CLEANSING POWER OF SOAP.

BY H. W. HILLYER.

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CHEVREUL, the first to study the fats and soaps, discovered that when soaps are acted on by water they are hydrolyzed to free alkali and to an acid salt. The tendency of the reaction may be expressed by the equation

$$NaAc + H_2O = NaOH + HAc,$$

where Ac stands for the palmitic or stearic acid radical. The acid thus set free unites with more or less of the undecomposed soap to form difficultly soluble acid salts which contain more and more acid in proportion to the alkali as the dilution of the solutions from which the salts separate increases.

Rotondi, basing his conclusions on a mixed soap, decided that when water acts on the soaps, there is formed an acid salt which is soluble with difficulty in cold water and a basic salt which is easily soluble. Recent work by Krafft and his co-workers[1] have shown that Chevreul was correct and that Rotondi fell into error, prob-

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[1] *Ber. d. chem. Ges.*, **27**, 1747; *Ibid.*, **27**, 1755.