Using the average ester values obtained and the usual formula $x=\frac{100(1-n)}{m-n}$ for calculating the percentage of adulteration, we find that the three-quarters kauri varnish figures 85 per cent., and the half and half kauri and rosin 53 per cent. It would seem that this method is fairly satisfactory but requires experimentation by other observers before implicit trust can be placed in it.

In conclusion, the writer wishes to express his indebtedness to his various assistants and students, Messrs. Hammond, Sulzer, Tufts, Merrill and Mason.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
September, 1906.

THE TECHNICAL DETERMINATION OF BENZENE IN ILLUMINATING GAS.[1]

BY D. A. MORTON.

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THE value of benzene vapor as a light producer in illuminating gas has led to its extensive use for enriching purposes, and its exact estimation in a simple way has become a matter of consequence.

Since 1 per cent. only in coke oven gas gives a lighting value of more than twelve candle-power, while 1 per cent. of ethylene gives less than one and one-half candle-power, there is a large difference in the lighting value of these constituents and their separate determination is necessary.

Although a number of methods have been proposed for the determination of benzene and some of these requiring long and careful manipulation are quite exact, none appears to be satisfactory for use in technical work where a simple and rapid, as well as reasonably accurate, test is desired.

W. Misteli,[2] in a recent review, cites the method of Haber and Oechelhaeuser[3] as being the only one suitable for testing small quantities of gas, yet even this method does not compare in rapidity and simplicity with the ordinary volumetric tests in technical analyses. The gist of the method is the absorption of the ethylene by bromine water and subsequent titration of the

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[1] Read at the Ithaca Meeting of the American Chemical Society.

[2] J. Gasbeleucht, Sept. 9, 1905, p. 804.

[3] Ber. 29, 2700.

excess of bromine. Benzene vapors, the authors claim, while dissolving completely or partially in the bromine water, do not unite chemically with the bromine and hence do not affect the titration. Only by long contact is there a slight reaction with the benzene. The difference between the ethylene found and the total illuminants is taken as the percentage of benzene.

The method of Dennis and O'Neill,[1] published in 1903, in which the benzene vapors are absorbed by shaking the gas in a pipette with ammonium nickel nitrate solution of prescribed strength, is, unlike the preceding method, simple and rapid and suitable in these respects for technical use. The nickel method was used for a considerable time in this laboratory because, on account of its convenience and supposed accuracy, it was presumed to be suitable for the purposes here required. Nevertheless on a number of occasions the tests were found to be incorrect and consequently a more exhaustive investigation of its merits was finally carried out, with results of such interest that we give them in detail below.

INVESTIGATION OF THE AMMONIUM NICKEL NITRATE METHOD.

The ammonium nickel nitrate solutions for the experiments were made up according to the directions given in the original article.[2] Both the regular solution and Geer's solution were tried, with identical results; and, since the solutions were made up by more than one analyst and at a number of different times, we cannot suppose the errors found in the tests to have been due to errors in preparing the solutions.

Following the directions of the authors in carrying out the tests, mixtures of benzene vapor and air were analyzed, 100 cc. of the gas mixture being shaken three minutes in an absorption pipette with the ammonium nickel nitrate solution, then three minutes in a second pipette with 5 cc. of 5 per cent. sulphuric acid over mercury to remove ammonia fumes. The decrease in volume by this treatment indicates the percentage of benzene.

Table "A" shows the results obtained. The percentage of benzene present in each case was determined by absorption with fuming sulphuric acid as in the regular way for illuminants. Besides the percentage of benzene present, and that found by the ammonium nickel nitrate test, the table gives the cubic centimeters

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[1] This Journal, 25, 503 (1903).

[2] Loc. cit., p. 505.

of benzene vapor previously absorbed by the reagent, for this has a decided influence, as will appear.

TABLE "A."

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Per cent. benzene present..	0.0	0.5	0.6	0.6	4.3	4.7	0.5	1.0	1.8	4.2
Per cent. benzene found...	—1.1	0.0	0.1	0.3	3.3	3.2	0.35	0.7	1.4	3.7
Benzene vapor previously absorbed, cc................	17.	17.	17.	1.	8.	12.	0.	0.	0.	0.

A glance at these results shows that the absorbing solutions must be perfectly fresh to obtain results that are even approximately correct. In tests 2 to 6, although at most only a small quantity of benzene vapor had previously been absorbed, in no case has more than three-fourths the benzene actually present been found by the test. In 1, 100 cc. of air, shaken with the reagent and the 5 per cent. sulphuric acid, has its volume *increased* to 101.1 cc.

If fresh ammonium nickel nitrate solution and fresh 5 per cent. sulphuric acid are used for each test (7 to 10) the results are better, though still too low by several tenths of 1 per cent. In technical works where complete analyses have sometimes to be made as frequently as once an hour, refilling the pipettes with fresh solutions for every test is an inconvenience that is best avoided. An improvement has been made in the laboratory of the Detroit Solvay works where the gas mixture is shaken three minutes in each of two ammonium nickel nitrate pipettes, thus keeping the contents of the second pipette comparatively fresh for some time.

On further examination we find not only that the ammonium nickel nitrate solution is an indifferent absorbent for benzene, but also that the absorbing power it does possess is due, *not to the nickel compound but to the water present.* That either water alone or dilute aqua ammonia gives practically the same results as the ammonium nickel nitrate solution is shown in the table of comparative tests given below.

Table "B" shows results from a number of tests made under conditions as nearly identical as possible in all comparative cases. In "I" fresh absorbing solutions were used. The gas taken for the test was air containing benzene vapor. One hundred cc. of the gas were passed into the absorbing pipette and shaken with the absorbent for the number of minutes indicated, drawn out and passed into a pipette of 5 per cent. sulphuric acid to remove fumes, then back into the burette, allowed the usual time to drain, and measured. In "II" the same conditions were observed except that the absorbing solutions were not fresh, having been used for the tests under "I." In "III" the gas in each case was shaken with the fresh reagent three minutes, then with 5 per cent. sulphuric acid three minutes, the tests all being made with especial care.

Table "C" shows the results of strictly comparative tests of the absorbing power of ammonium nickel nitrate solutions and pure water. In each case exactly 118 cc. of the absorbing solution were shaken for the time stated with 100 cc. of the gas and the unabsorbed residue drawn slowly back into the burette and measured. The gas was drawn back slowly to insure complete absorption of all ammonia fumes. (One hundred cc. of air passed into the fresh ammonium nickel nitrate solution, shaken one minute and drawn back in the same way remeasured exactly 100 cc.) Temperatures were the same, 18–19°, in all instances. In each case the gas tested was a mixture of air and a known quantity of benzene vapor.

TABLE "B."

"I."

Absorbing solution.	Am. Ni. nitrate.	Aqua ammonia (Sp. gr. 0.95).	Water.
Minutes shaken	3	2	3
Per cent. benzene present	9.9	9.9	9.5
Per cent. benzene found	9.0	8.8	8.1
Benzene vapor previously absorbed	0	0	0
"II."			
Minutes shaken	3	3	3
Per cent. benzene present	9.9	9.9	8.4
Per cent. benzene found	8.0	8.2	7.4
Benzene vapor previously absorbed, cc.	9.0	8.8	8.1

"III."

Number of test.	1.	2.	3.	4.	5.	6.
Per cent. benzene present	0.5	1.0	1.8	4.15	3.95	4.15
Per cent. benzene by Am. Ni. nitrate	0.35	0.7	1.4	3.65	.....	3.6
Per cent. benzene by water	0.4	0.8	1.5	3.4	3.5	3.35

TABLE "C."

Series.	Absorbing solution.	Minutes shaken.	Per cent. benzene found.	Per cent. benzene present.	Cc. benzene previously absorbed.
I.	Am. Ni. nitrate	2	6.1	7.2	0
	Water	2	6.0	7.2	0
II.	Am. Ni. nitrate	3	2.3	3.6	6
	Water	3	2.3	3.6	6
III.	Am. Ni. nitrate	2	0.4	1.0	0
	Water	2	0.4	1.0	0

From the above results we can draw no other conclusion than that in the determination by ammonium nickel nitrate solution, the benzene vapor is simply dissolved to a certain extent by the water in the solution—perhaps increased slightly by the ammonia in the case of the high percentages—but that the presence of the nickel compound has no appreciable influence whatever.

It would answer better to simply use fresh water each time as the solution for absorbing benzene and, if used under proper conditions, good results could perhaps be obtained with this reagent. Nevertheless the use of a fresh solution, even water, for every test involves certain inconveniences and liabilities to error and would be objectionable in technical practice.

By the use of concentrated sulphuric acid for the benzene absorption a better method is obtained. This method is reliable and convenient, and the results by it are so comparatively accurate that we have no hesitation in recommending it for the technical analysis of coal gases.

THE CONCENTRATED SULPHURIC ACID METHOD.

The marked solubility of benzene vapor in water (see Tables "B" and "C" above) renders necessary certain precautions in sampling and handling the gas previous to the test. If taken over water, the sample bottle should be completely filled with the gas, driving out practically all of the water, as otherwise some of the benzene will be absorbed.

After the determination of the carbon dioxide in the gas, by absorption in strong caustic soda[1] or potash solution in the usual manner, the benzene test is accomplished as follows:

The gas residue is passed into an ordinary simple absorption pipette containing concentrated sulphuric acid (sp. gr. 1.84)[2] and shaken *vigorously* with this reagent for one minute, by which treatment the benzene vapors are absorbed. The shaking is satisfactorily accomplished by giving a quick sharp motion to the pipette in such a way as to mix the contents thoroughly about twice per second, during the specified one minute. It is essential to shake vigorously with the sulphuric acid as directed, for the last traces of benzene are absorbed slowly and require thorough contact with the acid.

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[1] Caustic soda solution dissolves benzene to only a very slight extent, and the error caused thereby is negligible.

[2] Slight dilution of this acid does not detract from its efficiency, but the dilution should not exceed 2 per cent.

Experimental data on the conduct of concentrated sulphuric acid as an absorbent for benzene are given in the tables below.

Table "D" shows results obtained with mixtures of benzene and air. Good results are obtained even when more than 7 per cent. of benzene—a very high amount—is present.

Table "E" gives results showing that the concentrated sulphuric acid can be used for a large number of tests without renewal. The benzene combines with the sulphuric acid and is not removed by air subsequently introduced.

Table "F" shows the action of concentrated sulphuric acid on benzene-ethylene-air mixtures. The benzene is determined by the concentrated sulphuric acid test; the ethylene immediately afterward by fuming sulphuric acid in the usual way. In this table a slight defect in the method appears, due to the absorption of a trace of ethylene by the concentrated sulphuric acid. Higher homologues of ethylene would be absorbed to a greater extent than ethylene itself. The error diminishes rapidly as the percentage of benzene increases, becoming practically nil when 1 per cent. or more of the latter is present and probably not exceeding 0.2 per cent. in the case of any coal gas.

Table "G" shows the cubic centimeters of ethylene absorbed by the concentrated sulphuric acid test, per 100 cc. of gas, having given the percentage of benzene and ethylene present. By use of these data correction for the error can be made when desirable.

TABLE "D."

Benzene-Air Mixtures.

Number of test.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Per cent. benzene present...	0.5	0.6	0.65	1.9	3.0	3.6	4.0	4.5	4.7	7.8
Per cent. benzene found.....	0.5	0.6	0.6	1.9	3.1	3.55	3.8	4.35	4.6	7.7

TABLE "E."

Benzene-Air Mixtures.

Gas tested.	Benzene-air.	Benzene-air.	Benzene-air.	Air.	Air.
Number of test.	1.	2.	3.	4.	5.
Benzene vapor previously absorbed, cc........................	55.	120.	150.	55.	100.
Per cent. benzene present......	1.9	3.0	4.5	0.0	0.0
Per cent. benzene found.........	1.9	3.1	4.3	0.0	0.0

TABLE "F."

Benzene-Ethylene-Air Mixture.

Number of test.	1.	2.	3.	4.	5.	6.	7.	8.	9.
Per cent. benzene present..	0.55	0.50	0.50	0.50	1.0	1.0	1.0	2.85	3.0
Per cent. benzene found.....	0.85	0.70	0.65	0.60	1.05	1.0	1.05	2.85	3.0
Per cent. ethylene present.	9.5	10.1	4.8	5.0	9.95	4.8	5.0	4.4	4.5
Per cent. ethylene found....	9.5	10.0	4.7	4.8	10.1	4.8	5.0	4.6	4.7

TABLE "G."

Cubic Centimeters Ethylene Absorbed in Benzene Test.

		Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.
Ethylene present		1.0	2.0	3.0	4.0	5.0	6.0
	Per cent.	cc.	cc.	cc.	cc.	cc.	cc.
Benzene present	0.0	0.05	0.10	0.10	0.15	0.20	0.25
Benzene present	0.5	0.00	0.05	0.05	0.10	0.10	0.15
Benzene present	1.0	0.00	0.00	0.00	0.05	0.05	0.10

CONCLUSIONS.

From the results obtained the unsatisfactory character of the ammonium nickel nitrate method is apparent. As pure water absorbs benzene to practically the same extent as the ammonium nickel nitrate solution, it appears that the method really depends on the solubility of benzene vapor in water, or ammoniated water, and that the presence of the nickel compound has no influence. The results by the method are inaccurate and vary widely according to the amount of benzene in the gas and the quantity already present in the absorbing solution.

Concentrated sulphuric acid, on the other hand, absorbs benzene vapor as readily as could be desired, and can be used for a large number of tests without renewal, giving as accurate results after a hundred tests as when first prepared. The defect due to the absorption of ethylene is insignificant but may be easily corrected for (see Table "G"). Traces of the higher olefines, however, may give a value slightly too high for the benzene percentage, though this error, as shown by our tests of rich and lean gases from a variety of coals, must be small, if not inappreciable.

LABORATORY OF THE SOLVAY PROCESS CO.,
SYRACUSE, N. Y., June, 1906.

NOTE.

Solubilities of Permanganates of the Alkali Metals.—The article by Baxter, Boylston and Hubbard on "The Solubility of Potassium Permanganate,"[1] reminds the writer that in the course of some work on the preparation of various permanganates, at Johns Hopkins University in 1900, a few solubility determinations were made, the results of which have not been published except in his dissertation. They are reproduced below, together with some extracts from the dissertation. The permanganates of rubidium and caesium were made by neutralizing the pure

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[1] This Journal, 28, 1336.