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DETERMINATION OF BENZENE IN BITUMINOUS MATERIALS

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INTRODUCTION

Workers with bituminous materials such as asphalts, road oils and allied substances frequently have occasion to desire estimates of amounts of benzene contained in these materials. Such estimates are often of value when dealing with original products, as affording additional information on their complex nature. In addition, when asphalts or road oils are extracted with benzene and recovered, it becomes of importance to know whether the recovery process has removed all the benzene used in the extraction, the presence of benzene in trace amounts having a profound effect on the viscosities and other properties of asphaltic fluids.

The significance of failure to remove all benzene during asphaltic recoveries has been appreciated for some time, and as early as 1940 the Research Laboratory of the Michigan State Highway Department had developed a procedure (1) for detecting the presence of small amounts of this compound. The technique employed involved conversion of any benzene present to nitrobenzene, which was identified by odor. Conversion of the nitrobenzene to aniline, with estimation of the latter by a color reaction with bleaching powder, was reported for quantitative determinations.

Certain weaknesses of the above method, however, led to a search for a more reliable procedure. It was felt that the method was too involved, that use was made of too many chemical conversions, and that quantitative accuracy could be attained only with great difficulty.

In 1943, S. M. Dolin (2) reported a method of determining benzene colorimetrically in the presence of its homologs. Dolin's technique employs only one conversion directly to m-dinitrobenzene. This conversion is quantitative, and the m-dinitrobenzene is estimated by the intensity of the crimson color produced with butanone (methyl ethyl ketone) in alcoholic sodium hydroxide solution. Color comparisons can be made visually, or a photoelectric colorimeter may be used. The test is absolutely specific, benzene being the only substance which will produce the reaction.

Accordingly, Dolin's test was studied to determine its suitability for the estimation of benzene in recovered road oils. It was found that the test was suitable, provided certain modifications were made.

The first modification deals with Dolin's method of converting benzene to m-dinitrobenzene. For some reason, Dolin's report erroneously describes a nitrating procedure which, if followed, converts benzene quantitatively into nitrobenzene instead of m-dinitrobenzene. In order to convert to m-dinitrobenzene, it was found necessary to begin nitration at room temperature instead of 0° to -5°C. as recommended in Dolin's report. This, if anything, simplifies the procedure.

The second modification concerns the removal of the m-dinitrobenzene from such bituminous products as asphaltenes, carbenes and carboids, whose presence interferes with subsequent steps in the procedure. It was found that this removal could be accomplished satisfactorily by ten cycles of aqueous washing in a Soxhlet extractor.

Dolin's test was further simplified by eliminating the necessity for final acidification with acetic acid.

REAGENTS AND APPARATUS

Nitrating mixture, equal parts by volume of fuming nitric acid, specific gravity 1.49 to 1.50, and concentrated sulfuric acid, specific gravity 1.84.

Sodium hydroxide, aqueous, 1 volume of 40 per cent sodium hydroxide diluted to 4 volumes with distilled water.

Sodium hydroxide, alcoholic, made by diluting 1 volume of 40 per cent sodium hydroxide to 10 volumes with 95 per cent ethyl alcohol and filtering or decanting just prior to use.

Butanone (methyl-ethyl ketone), practical grade.

Alcohol, ethyl, pure, 95 per cent.

Kerosene (refined).

Set of test tubes of about 50-ml. capacity. These tubes should be of the same diameter (2 cm.) and of equal transparency.

Soxhlet extractor.

Photoelectric colorimeter (advantageous, but not essential).

Pipets graduated to 0.01 ml.; also 10 ml. pipet.

Buret, 50 ml.

Separatory funnel, ca. 325 ml.

Volumetric flasks, 50 ml. and 100 ml.

PROCEDURE

A portion of the bituminous material to be tested shall be dissolved in kerosene so that 1 ml. of solution contains 0.5 gm. of the bituminous material. A 0.50 ml. portion of this solution is measured into a 125 ml. Erlenmeyer flask. Nitrating mixture from a buret is added to the solution, starting at room temperature, at the rate of 2 drops per second while the flask is rotated. After 10 ml. have been added, the flask and contents, now warm from the reaction, are removed from under the buret and 35 ml. distilled water are added. This causes boiling and evolution of oxides of nitrogen. Warning: nitration and dilution should be done under an adequately ventilated hood.

The resulting mixture is filtered while still hot into the Pyrex flask of the Soxhlet-Allihn extraction assembly (Figure 1). After filtration, the filter paper is carefully removed from the funnel and transferred to the extractor. The funnel is washed and removed, and the flask connected to the extractor. Approximately 50 ml. distilled water are poured down the condenser into the filter paper in the extractor. The burner is turned on and extraction is continued until 10 washings of the filter paper have siphoned over.

The flask and contents are cooled to room temperature and the extract washed quantitatively into the separatory funnel. The m-dinitrobenzene is extracted with ether, by shaking the mixture with 25 ml. of ether and repeating the extraction of the aqueous layer three times with 10 ml. of ether each (See Figure 2).

The combined ether solutions are next washed by shaking with 10 ml. of aqueous sodium hydroxide reagent in the separatory funnel, followed by two consecutive washings with 10 ml. portions of distilled water.

The washed ether solution is transferred to a 100 ml. volumetric flask and filled to the mark with 95 per cent alcohol. A 10 ml. aliquot of this solution is pipetted into a 50 ml. volumetric flask, and alcohol added to the 50 ml. mark.

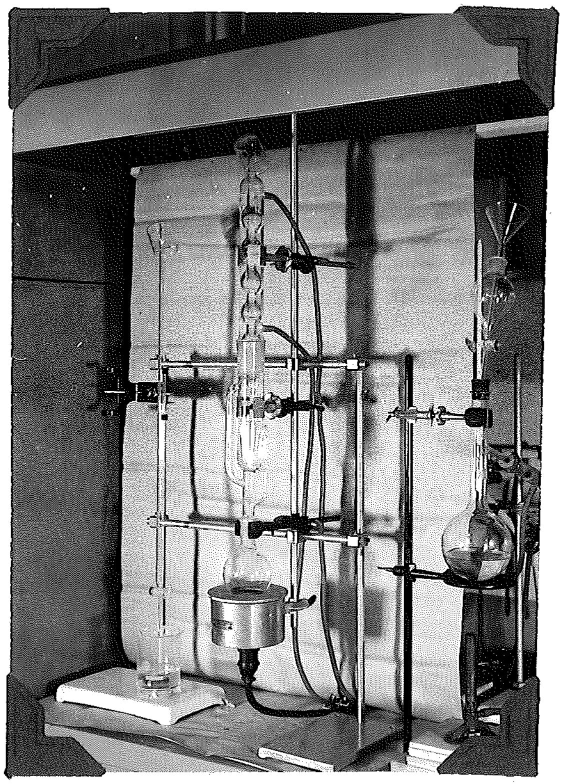


Figure 1

Soxhlet-Allihn extraction assembly used in performing hot aqueous extractions of m-dinitrobenzene. Nitration is carried on under buret at extreme left. Alcohol recovery apparatus at right.

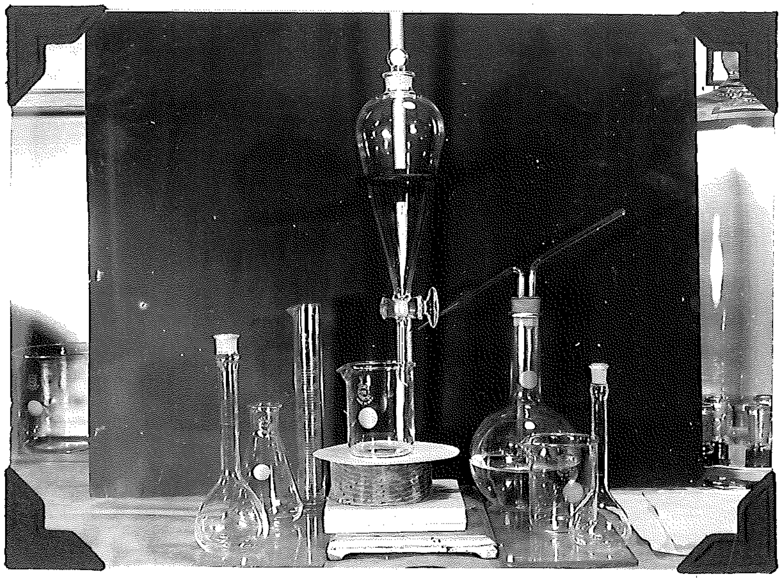


Figure 2. Ether extraction apparatus used in performing ether extractions of m-dinitrobenzene.

A 10 ml. portion of the last solution is now pipetted into one of the set of similar 50 ml. test tubes. Exactly 1.0 ml. of butanone is added, followed by 1.0 ml. of alcoholic sodium hydroxide reagent. The tube is agitated immediately and the intensity of the crimson color is measured 10 minutes after agitation.

The intensity of the color may be measured by visual comparison in a simple color comparator, in accordance with standard principles of colorimetry, with the color produced in a second similar solution containing a known amount of benzene and carried through the same steps simultaneously with the first solution. Or, a standard visual or optical type colorimeter may be used to compare the intensities of the two colors.

The necessity of a second solution containing a known quantity of benzene may be eliminated, however, by use of a photoelectric colorimeter (Figure 3) with a green filter and reference to the concentration curve, Figure 4. This curve was prepared with the aid of a Central Scientific Co. Cenco-Sheard-Sanford Photelometer, using Cenco green filter No. 2, but should be accurate for use with any comparable apparatus.

Distilled water is used as a reference solution, and No. 12338-A (1 cm.) Cenco fused chemical glass absorption cells are employed. The potentiometer needle is brought to 100 with distilled water, and the reading through the crimson solution is noted. When this reading is found on the abscissa, the ordinate gives the amount of benzene present in the sample of asphaltic oil, in ml. of benzene per gram of oil.

DISCUSSION

The solubility of m-dinitrobenzene in water is 0.3 gm. solute to 100 gm. water at 99°C. This material is much less soluble in water at room

Figure 3. Photoelectric colorimeter suitable for estimating quantities of m-dinitrobenzene. Electric leads are from power supply beneath table.

temperature, hence the necessity of using a Soxhlet extractor and employing at least 10 cycles of extraction in the boiling solvent. This nitrated material is very soluble in both alcohol and ether, but so, unfortunately, are materials present in the nitrated mixture of hydrocarbons. The separation, then, is best performed by repeated leaching with hot water.

Inasmuch as ethyl ether is soluble in water to the extent of 7.5 gm. ether for every 100 gm. of water at 20°C., the subsequent separations with ether must be limited to the minimum quantities of this solvent specified in the procedure.

Kerosene is used as a solvent for the bituminous material to be tested, first, because of certain features of kerosene which makes this a suitable solvent, and secondly, because of the difficulty of weighing small quantities of asphaltic oil accurately. It is much easier to weigh out larger quantities and take aliquot portions of their solutions volumetrically. It is the use of kerosene which establishes the point of zero concentration of benzene at 90 per cent transmission on the curve in Figure 1 rather than at 100 per cent. Therefore, although Lambert's law is followed exactly, Beer's law is followed only after an initial lag of approximately 10% absorption.

Lambert's Law:

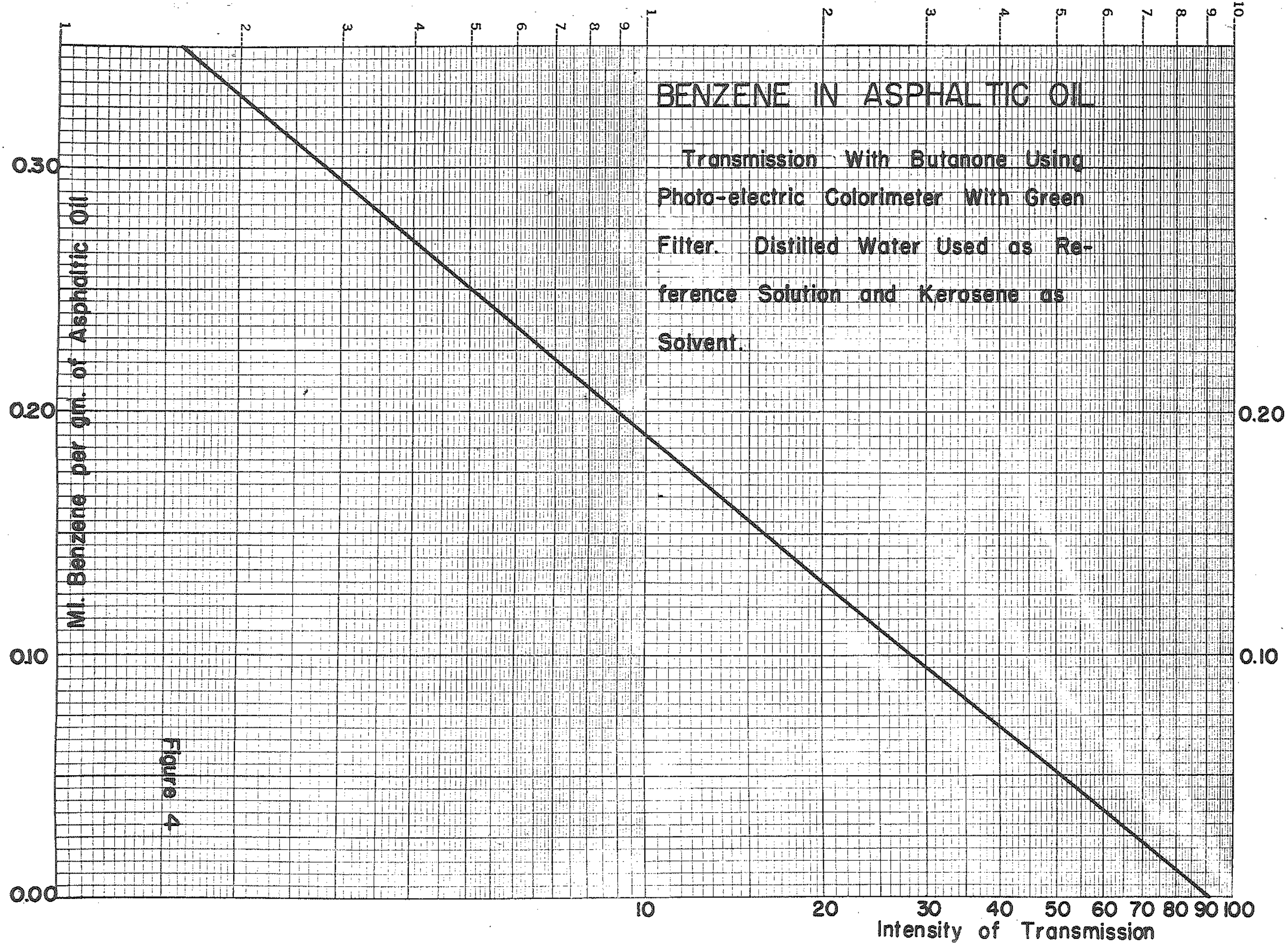
$$I = I_o e \quad - \quad l$$

Beer's Law:

$$I = I_o \quad - cl$$

I_o = intensity of light entering crimson solution.

I = intensity of light after passing through "l" cms.



BENZENE IN ASPHALTIC OIL

Transmission With Butanone Using Photo-electric Colorimeter With Green Filter. Distilled Water Used as Reference Solution and Kerosene as Solvent.

Figure 4

μ = absorption coefficient of the solution.

α = A constant for the absorbing solute and is the ratio of "the transmitted to the incident intensity for unit thickness and unit concentration."

l = length of path in cms.

c = concentration of absorbing material in solution expressed in gram-molecules per liter.

Inasmuch as the intensity of the crimson color reaches a peak in ten minutes and then slowly fades, it is essential that readings be taken ten minutes after addition of the last reagent.

This test is extremely sensitive (2), 1×10^{-6} ml. of benzene giving a recognizable response.

REFERENCES

(1) E. A. Finney and Thaddeus Wolczynski, "Changes in Characteristics of Slow-Curing Asphaltic Oils", *Proceedings of the Association of Asphalt Paving Technologists*, Vol. 12, p. 264, 1940.

(2) B. H. Dolin, "Determination of Benzene", *Industrial and Engineering Chemistry, Analytical Edition*, Vol. 15, No. 4. pp. 242-7, April 15, 1943.