±2.1 p.p.m. of the true value better than 99 times out of 100. This is also an indication of the sensitivity, in that a single determination might show no glyoxalidine when, in fact, 2 p.p.m. are actually present. However, if a number of determinations are made on samples from the same batch, there is good assurance that a sensitivity of 1 p.p.m. or less might be achieved.

Synthetic samples also were prepared from canned cherries, using fruit known to be free from glyoxalidine residues. The amount of pure heptadecylglyoxalidine added and that recovered by analysis are shown in Table II.

In the case of samples A to E, application of the *t* test at the 1% level of probability indicates a significantly low recovery. This is probably due to the introduction of a constant error—e.g., in the preparation of the synthetic samples. The high recoveries obtained on samples G and H indicate that the modified procedure is inherently as accurate as that used for the analysis of apples.

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Determination of Divinylbenzene in Dehydrogenated Diethylbenzene

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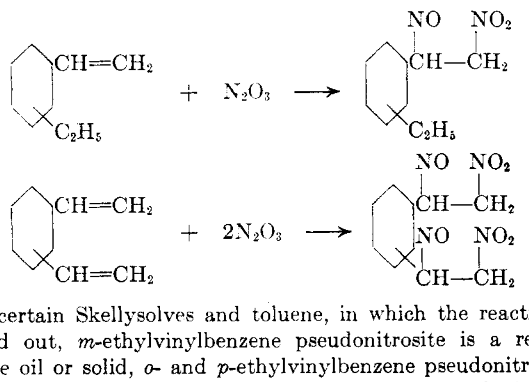
SOMMER (*4*) in 1895 reported that styrene reacted with nitrous oxide to form the styrene nitrosite. Wieland (*6*) in 1903 verified Sommer's observation. Little if any information is reported in the literature about the reaction of nitrous oxide with ethylvinylbenzene and divinylbenzene. Wallach (*5*) identified various terpenes by means of the physical properties of their crystalline nitrosites produced by the addition of nitrous oxide to the double bonds. Bond (*1*) developed a method for the gravimetric determination of styrene as the styrene nitrosite in various gasoline fractions; his procedure for producing the nitrosites in a Tutwiler buret was adapted with modifications for the determination of divinylbenzene as described in this paper.

OUTLINE OF METHOD

The main constituents of dehydrogenated diethylbenzene are divinylbenzene, ethylvinylbenzene, and diethylbenzene.

Nitrous oxide, produced by the addition of dilute sulfuric acid to an aqueous solution of sodium nitrite, is added to the double bonds of the dehydrogenated diethylbenzene to form the pseudonitrosites (*3*). The reaction with ethylvinylbenzene and divinylbenzene under the conditions outlined is probably as follows:



In certain Skellysolves and toluene, in which the reaction is carried out, *m*-ethylvinylbenzene pseudonitrosite is a readily soluble oil or solid, *o*- and *p*-ethylvinylbenzene pseudonitrosites are soluble crystalline solids, and divinylbenzene pseudonitrosite is an insoluble solid which is filtered off, dried in vacuum, and weighed. The per cent divinylbenzene is then read from a graph prepared by the analysis of known solutions of divinylbenzene in diethylbenzene and ethylvinylbenzene.

REAGENTS

Sodium Nitrite. Prepare a saturated solution by dissolving 144 grams of sodium nitrite in 168 ml. of water.

Sulfuric Acid. Dissolve 1 volume of concentrated sulfuric acid in 4 volumes of water.

Skellysolve C. A mixture of aliphatic hydrocarbons having a boiling range of 86° to 100° C.

Skellysolve F. A petroleum ether having a boiling range of 30° to 60° C.

Toluene, technical grade.

Acetone, technical grade.

APPARATUS

Tutwiler buret, 100-ml. size, having a 3- to 4-mm. bore lower stopcock.

Vacuum pump fitted with a manometer and drying tower filled with Ascarite.

Fritted glass crucibles, 30-ml. size and medium porosity, with a 30-ml. Griffin beaker which will fit inside the crucible.

Vacuum desiccator, filled with anhydrous calcium chloride.

Inasmuch as divinylbenzene has found an increasing use in various manufacturing processes and is produced by the dehydrogenation of diethylbenzene, a direct analytical method for determining this product in the presence of other unsaturates is desirable. A procedure was developed in which nitrous oxide is added to the double bonds, producing the pseudonitrosites. Under the conditions described, only the pseudonitrosite of divinylbenzene precipitates; it is determined gravimetrically. The per cent divinylbenzene is read from a graph prepared from data obtained by analysis of known solutions. The accuracy of the method is within ±0.5% of the absolute value. As far as is known, the described procedure is the only one available for the direct determination of divinylbenzene in the presence of other unsaturates, especially styrene and styrene derivatives such as α-methylstyrene and isomers of ethylvinylbenzene.

Table I. Data Used for Preparation of Figure 1

Known	% DVB	Pseudonitrosite, Grams (0.5-Gram Sample)	Pseudonitrosite, Av. Grams (0.5-Gram Sample)
1	98.7	1.0423, 1.0510, 1.0385	1.044
2	79.73	0.8814, 0.8649	0.873
3	60.29	0.6855, 0.6748	0.680
4	40.81	0.4564, 0.4520	0.454
8	31.31	0.3409, 0.3365, 0.3349	0.337
5	20.62	0.1815, 0.1876	0.185
6	10.40	0.0622, 0.0610	0.0616
7	3.24	0.0043, 0.0044	0.0044
9	Nil	0.0023, 0.0022	0.0023

PROCEDURE

Place an accurately weighed 0.99- to 1.01-gram sample of dehydrogenated diethylbenzene in a 50-ml. glass-stoppered volumetric flask and make to volume with Skellysolve C.

Evacuate the bulb of the Tutwiler buret, pour 10 ml. of saturated aqueous sodium nitrite into the graduated part of the Tutwiler buret, and draw the solution into the bulb. Wash out the graduated buret with water. Evacuate and pipet a 25-ml. aliquot of the sample into the bulb. Then add 25 ml. of toluene.

Fill the graduated buret with dilute sulfuric acid. Evacuate the bulb to 12 cm. of pressure, add 1 to 2 ml. of sulfuric acid to the contents of the bulb, and shake vigorously. After all the liberated nitrous oxide has reacted with the dehydrogenated diethylbenzene, add about 1 ml. of sulfuric acid and shake the buret again. Continue adding similar portions of sulfuric acid and shaking the buret until a pressure develops in the bulb.

Release the pressure, re-evacuate to 12 cm. of pressure, and continue the addition of 1- to 2-ml. portions of sulfuric acid until a pressure develops again.

Repeat the above operation for the third time; then remove the excess sulfuric acid and wash the graduated buret with water.

Caution. Wear goggles while adding the sulfuric acid, as it is possible to develop enough pressure to loosen the stopcocks and spray out the contents of the buret. After a little practice, however, this rarely happens.

Filter off the precipitate using a fritted-glass crucible which has been tared with a 30-ml. beaker. Wash the bulb of the buret with 10 ml. of water and then add the water to the precipitate. Masticate the precipitate thoroughly with a rubber policeman and filter off the water. Repeat three times with 10-ml. portions of water.

Wash the bulb of the buret and masticate the precipitate with 10-ml. portions of Skellysolve F as was done with the water. Filter off the wash solution. Repeat with two more 10-ml. portions of Skellysolve F. Wipe the crucible clean and dry overnight in the vacuum desiccator.

Dissolve the precipitate remaining in the bulb of the buret with 2 to 3 ml. of acetone and pour the solution into the 30-ml. beaker that was tared with the crucible. Wash twice with similar portions of acetone and combine the washings with those in the beaker. Dissolve any precipitate remaining on the rubber policeman with acetone and add to the washings. Evaporate the solvent and dry the beaker at a temperature not over 35° C.

Place the beaker in the crucible on top of the precipitate of divinylbenzene pseudonitrosite and weigh. Obtain the net weight of divinylbenzene pseudonitrosite.

CALCULATION

Calculate the per cent divinylbenzene in the sample in the following manner:

$$\frac{\text{Net wt. of divinylbenzene pseudonitrosite}}{\text{sample wt.}} = \text{wt. of}$$

divinylbenzene pseudonitrosite per 0.5000-gram sample

Read the per cent (by weight) divinylbenzene from the graph.

PREPARATION OF GRAPH

The divinylbenzene used titrated 201.8% as ethylvinylbenzene by the mercuric acetate method for determining unsaturation (*2*). Infrared analysis showed but a small amount of ethyl group present. Assuming this ethyl group to be present as ethylvinylbenzene, the only major impurity, the calculated composition of the sample was 98.7% divinylbenzene and 1.3% ethylvinylbenzene. The meta isomers of the two compounds predominated.

The *m*-ethylvinylbenzene assayed 99.7% as determined by the freezing point method. The diethylbenzene was plant grade, predominantly the meta isomer, and free of unsaturation.

Equal volumes of *m*-ethylvinylbenzene and diethylbenzene were mixed together making a solution considered to contain less than 0.1% divinylbenzene. Solutions containing known concentrations of divinylbenzene were then prepared by diluting weighed portions of the 98.7% sample of divinylbenzene with weighed portions of this 50-50 solution.

The known solutions were then analyzed by the described procedure and the data for the graph, Figure 1, as shown in Table I, were obtained.

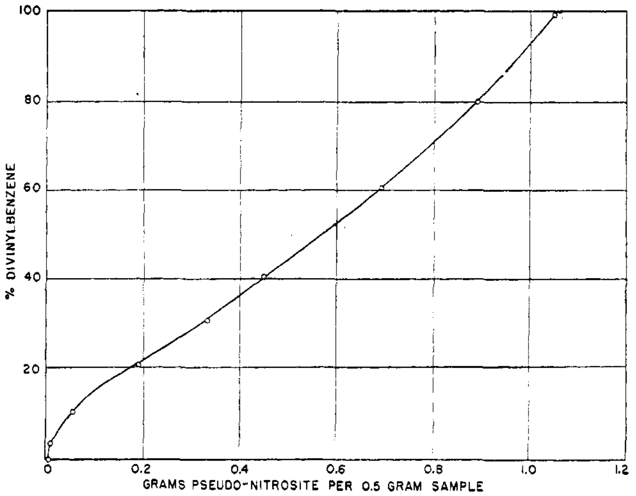


Figure 1. Standard Curve for Per Cent Divinylbenzene

The per cent divinylbenzene versus grams of divinylbenzene pseudonitrosite were plotted on ordinary coordinate graph paper.

ANALYTICAL DATA

To test the analytical procedure for reproducibility of results for divinylbenzene, several samples of known concentrations of the 98.7% divinylbenzene in the 50-50 solution of *m*-ethylvinylbenzene were prepared. These knowns were analyzed by the described procedure and the per cent divinylbenzene was read from the graph. The analytical results obtained are shown in Table II.

INTERFERENCE OF ISOMERS AND OTHER STYRENES

When this analytical procedure was used on 99.7% *m*-ethylvinylbenzene, 0.0018-gram of precipitate per 0.5000-gram sample, equivalent to 0% divinylbenzene, was obtained. Thus, this compound does not interfere in any concentration.

α-Methylstyrene, 98.6% by mercuric acetate procedure, gave only 0.0013 gram precipitate per 0.5000-gram sample equivalent to 0% divinylbenzene, and thus likewise provides no interference.

With 99.1% *o*-ethylvinylbenzene and 99.7% *p*-ethylvinylbenzene, as determined by the freezing point method, 0.1577 and 0.3796 gram of precipitate, equivalent to 18.6 and 34.7% divinylbenzene, respectively, were obtained from 0.5000-gram samples. These results showed that the pseudonitrosites of these isomers are sparingly soluble in the solvent mixture and will interfere with the determination of divinylbenzene if present in too high a concentration.

Similarly, styrene, 99.6% by freezing point method, produced 0.6510-gram precipitate per 0.5000-gram sample, and will thus interfere if present in too large amounts.

To determine how much *o*-ethylvinylbenzene, *p*-ethylvinylbenzene, and styrene may be present before erroneous results are obtained, known amounts of these compounds were added to dehydrogenated diethylbenzene containing 49.0% divinylbenzene, and analyzed. The results are shown in Table III.

Thus, for samples containing 25 to 30% or more of divinylbenzene, at least 40% of either *o*-ethylvinylbenzene or *p*-ethylvinylbenzene may be present without affecting the analytical results. Likewise, almost 10% of styrene may be tolerated. A combined total of at least 40% of the ortho and para isomers of ethylvinylbenzene and 5% of styrene may be present in similar concentrations of divinylbenzene without interference.

However, for low percentages of divinylbenzene, these compounds should be present in smaller amounts to be sure of no interference. Table IV shows results with known solutions of these compounds in diethylbenzene; amounts shown in known 6, Table IV, may be considered safe maximum limits.

An explanation of why larger amounts of styrene, *o*-ethylvinylbenzene, and *p*-ethylvinylbenzene may be present without analytical interference in the samples containing over 25% divinylbenzene than in the samples containing little or no divinylbenzene, as shown by the data in Tables III and IV, has not been verified by experiment.

A 10.2% solution of divinylbenzene made by diluting a portion of the 49.0% sample with diethylbenzene, and a 10.0% solution made by diluting another portion of the same sample with *m*-ethylvinylbenzene, were prepared. On analysis by this procedure, the known solutions were found to contain 9.6, 9.2, 9.7, and 9.2% divinylbenzene, respectively. This indicates that variations in the ratio of *m*-ethylvinylbenzene to diethylbenzene do not materially affect the results for divinylbenzene.

Table II. Analysis of Known Divinylbenzene Solutions

Known	% DVB	Pseudonitrosite, Gram (0.5-Gram Sample)	% DVB from Graph
1	6.4	0.0174 0.0191 0.0198	6.0 6.2 6.3
2	15.9	0.121 0.132 0.122	15.7 16.5 15.8
3	35.8	0.391 0.402 0.401	35.6 36.5 36.4
4	44.2	0.508 0.500 0.502	45.1 44.5 44.6
5	66.7	0.740 0.734 0.745	66.1 65.4 66.5
6	86.5	0.940 0.942 0.937	86.8 87.1 86.6

Table III. Analysis of Divinylbenzene Solutions Containing *o*-Ethylvinylbenzene, *p*-Ethylvinylbenzene, and Styrene

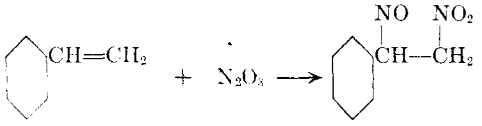
Known	99.05% *o*-EVB Added, % *o*-EVB	99.7% *p*-EVB Added, % *p*-EVB	99.6% Styrene Added, % Styrene	DVB Present, %	DVB Found, %
Dehydrogenated DEB	...	...	...	..	49.0
1	9.97	...	...	44.1	43.8 43.8
2	...	9.91	...	44.1	43.9 43.5
3	20.4	...	...	38.9	37.8 38.6
4	...	19.7	...	39.3	39.7 39.4
5	39.8	...	...	29.3	28.7 29.5
6	...	39.4	...	29.6	29.8 29.7
7	...	...	10.00	44.1	45.0 45.5
8	...	...	5.4	46.4	46.4 46.2
9	20.1	19.4	5.4	26.9	26.3 26.3

Table IV. Analysis of Diethylbenzene Solutions Containing *o*-Ethylvinylbenzene, *p*-Ethylvinylbenzene, and Styrene

Known	99.05% *o*-EVB Added, % *o*-EVB	99.7% *p*-EVB Added, % *p*-EVB	99.6% Styrene Added, % Styrene	DVB Present, %	DVB Found, %
1	40.81	..	..	Nil	Nil
2	...	40.1	..	Nil	6.3 5.8
3	...	..	10.7	Nil	4.4 4.1
4	...	..	5.5	Nil	Nil
5	20.1	19.7	5.6	Nil	8.0 8.0
6	10.2	7.8	2.0	Nil	Nil

DISCUSSION

With styrene, it is believed that the principal product is the pseudonitrosite (*3, 6*):



Analysis of the pseudonitrosite of styrene showed that 14.5% nitrogen was present, which is somewhat less than the theoretical value of 15.6%. Theoretical per cent nitrogen for the pseudonitrosite of the ethylvinylbenzene is 13.5; for the pseudonitrosites of *o*-ethylvinylbenzene and *p*-ethylvinylbenzene, the per cents nitrogen found were 12.6 and 13.4, respectively. Theory for the pseudonitrosite of divinylbenzene is 19.9 whereas the per cent nitrogen actually found was only 16.2. Inasmuch as several days elapsed between the preparation and the analysis of most of these pseudonitrosites, the low results for nitrogen are probably due to the slow decomposition of these compounds at room temperature. A closed bottle containing these compounds often will have oxides of nitrogen in it after a period of time.

As the pure isomers of divinylbenzene were not available (the dehydrogenated diethylbenzene contains over 70% of meta isomers) it was not determined whether equal amounts of each of the three possible isomers of divinylbenzene would yield the same weight of precipitate with the addition of nitrous oxide. However, it is believed that the difference, if any, would be negligible, and in most of the samples the meta isomer predominates uniformly.

Samples containing less than 6% divinylbenzene may be analyzed by first enriching with a known amount of divinylbenzene. The per cent of this compound in the original sample can then be calculated.

In general this method is applicable to the determination of divinylbenzene in the presence of many other olefinic compounds, especially styrene and styrene derivatives such as α-methylstyrene and the isomers of ethylvinylbenzene. The average value obtained from duplicate determinations by this method can reasonably be expected to determine the per cent divinylbenzene in a sample of dehydrogenated diethylbenzene within ±0.5% of the absolute value.

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