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DIETHYLPHTHALATE II.

BY J. A. HANDY AND L. F. HOYT.

(Continued from p. 609, July number.)

III. TESTING FOR DIETHYLPHTHALATE IN BEVERAGES.

Preliminary tests on beverages, Table III, showed that the substances which react most similarly to diethylphthalate did not interfere with a correct interpretation of the diethylphthalate tests. Accordingly a series of alcoholic beverages containing various known amounts of diethylphthalate were subjected to the Handy-Hoyt and Calvert tests. Owing to lack of time the series of samples were not run

by the Andrew test, by which, however, the results of Table III indicate that results strictly parallel to those of the Handy-Hoyt method would be obtained.

Seven beverages were used, and 3 test samples of each beverage were prepared. One sample was the original beverage, containing no diethylphthalate, the second sample contained 1% by volume of 39-C alcohol (equiv. to 0.01% of diethylphthalate in the sample to be tested) and the third sample was made by mixing 9 vols. of the beverage with 1 vol. of 39-C alcohol (equiv. to 0.1% of ester in the sample to be tested). These 21 samples were marked in code so that the analyst did not know whether the individual sample contained 0.1%, 0.01% of diethylphthalate or none.

Preliminary tests were made to determine whether or not the fluorescein test could be properly made on the samples directly. Samples containing an appreciable amount of saccharine matter—such as a sweet wine—cannot be satisfactorily tested directly for diethylphthalate by the modified fluorescein test. The sugars that such samples contain caramelize and foam, causing trouble in the fusion and, in addition, give very dark reddish brown final solutions which often show a pseudo-fluorescence and in which the color of true fluorescein is masked unless diethylphthalate is present in large amounts. It was found by experiment that although as small an amount of diethylphthalate as 0.01% could be detected in whisky by direct test, the difference between such a test and a blank test on the same sample without the ester was so slight, due to interfering substances, as to be confusing to anyone who had not had considerable experience with the method.

Extraction of beverage samples with petroleum ether, as recommended by Lyons, eliminates the trouble from saccharine matter, tannins, etc., and such extracts do not usually contain enough volatile oils to interfere with the delicacy of the test. Hence in the detection of diethylphthalate in these beverage samples, all samples were extracted with petroleum ether.

Full directions for the manner in which the tests were made by the Handy and Hoyt method are as follows:

To 5 cc. of sample measured into a small separatory funnel, add 5 cc. distilled water and shake out this mixture with one 10-cc. portion of petroleum ether. Pour petroleum ether extract into a 3-inch evaporating dish containing 1 cc. of 10 per cent. NaOH solution and evaporate to dryness on a steam-bath. To the dry residue add 2 cc. of 1.84 H₂SO₄, and heat resulting syrupy solution one to two minutes on a steam-bath and pour into a dry test-tube containing 0.05 gram resorcin. Heat mixture for 3 minutes at 160° C., shaking at intervals to dissolve *all* the resorcin. Pour a portion of the melt into a mixture of 50 cc. of water and 10 cc. of 10 per cent. NaOH. A permanent, yellowish green fluorescence indicates the presence of diethylphthalate.

The above test was applied to the 21 samples of 7 beverages, prepared as previously described.

In the testing of the beverages some interesting points were brought out.

1. All of the 7 samples which contained 0.1% of diethylphthalate revealed its presence unmistakably to the sense of taste, though not to the same degree. In beer, cordial, and sweet wine, the bitter acrid taste of the ester was especially strong, while in the other beverages its presence (actually in the same amount) was not as noticeable. It was found impossible to differentiate with certainty by taste, between a beverage containing 0.01% of the ester and a "blank" of the same beverage containing none.

TABLE IV.—DETECTION OF DIETHYLPHTHALATE IN BEVERAGES BY THE HANDY AND HOYT METHOD

Sample marked.	Test: fluorescein color.	Conclusion: diethyl- phthalate. %	Sample actually con- tained diethylphthalate. %	Diagnosis.
Beer, 1	+, Faint	Present; 0.01	0.01	Correct
Beer, 2	++, Strong	Present; 0.1	0.1	Correct
Beer, 3	—, . . .	None	None	Correct
Sweet wine, 1	—, . . .	None	None	Correct
Sweet wine, 2	+, Faint	Present; 0.01	0.01	Correct
Sweet wine, 3	++, Strong	Present; 0.1	0.1	Correct
Sherry, 1	++, Strong	Present; 0.1	0.1	Correct
Sherry, 2	+, Faint	Present; 0.01	0.01	Correct
Sherry, 3	—, . . .	None	None	Correct
Apricot cordial, 1	+, Faint	Present; 0.01	0.01	Correct
Apricot cordial, 2	—, . . .	None	None	Correct
Apricot cordial, 3	++, Strong	Present; 0.1	0.1	Correct
Gin, 1	+, Faint	Present; 0.01	0.01	Correct
Gin, 2	—, . . .	None	None	Correct
Gin, 3	++, Strong	Present; 0.1	0.1	Correct
Bicarde rum, 1	—, . . .	None	None	Correct
Bicarde rum, 2	++, Strong	Present; 0.1	0.1	Correct
Bicarde rum, 3	+, Faint	Present; 0.01	0.01	Correct
Whisky, 1	++, Strong	Present; 0.1	0.1	Correct
Whisky, 2	—, . . .	None	None	Correct
Whisky, 3	+, Faint	Present; 0.01	0.01	Correct

2. The following interesting and very important fact was observed:

The 3 samples of whisky, when tested directly on 5-cc. portions (*i. e.*, without extraction with petroleum ether) gave final solutions all of which were rather dark colored as a result of the traces of carbohydrate present and all of which showed fluorescence. Whisky 1, containing 0.1% of diethylphthalate, gave an intense fluorescence and there was no doubt about the presence of the ester. Samples 2 and 3 showed very little difference between them at the time the final dilution was first made. *However, on standing for 2 days, fluorescence had entirely disappeared from the No. 2 sample test solution, whereas No. 1 still showed a distinct fluorescence.* There was then no difficulty whatever in positively differentiating these two tests, even though they had not been made on an extracted sample.

The same condition was observed in the cases of the tests made on the extracted samples of Gin, 1 and 2, which could not be differentiated when the dilutions were fresh, but on standing showed a marked difference which permitted a correct diagnosis as to their diethylphthalate content.

Over two months after the tests on the 21 beverage samples had been made by the Handy-Hoyt method the final test solutions were again examined. The test-tubes had stood on the laboratory table, unstoppered and hence exposed to sunlight and air. Without resorting to the original data in the notebook as to the conclusions arrived at when the samples were first tested, a new conclusion sheet was made out for the 21 samples based on the intensity of, or absence of, the fluorescence after this 2 months' standing. In every case the conclusions tallied with those originally arrived at and which were correct in each instance.

CALVERT TEST AS APPLIED TO THE DETECTION OF DIETHYLPHTHALATE IN BEVERAGES.

The 21 samples, 3 of each of 7 beverages previously described and containing either none, 0.01% or 0.1% of diethylphthalate, were all tested by the Calvert method, using the same sized samples as for the Handy-Hoyt test.

A 5-cc. sample of each beverage, diluted with 5 cc. of water, was extracted once with 10 cc. of petroleum ether. The ether extract was transferred to a test-tube, 6 drops phenol added and the petroleum ether evaporated by placing the test-tube in a steam-bath. As soon as the petroleum ether was entirely evaporated, 10 drops of 1.84 H₂SO₄ were added and the test completed in the usual way.

The result of these 21 tests by the Calvert method was unsatisfactory. In the samples which had contained 0.1% of diethylphthalate a positive test was obtained with each of the 7 beverages. The pink color produced, however, was unusually fugitive and in no case did the pink color, even when initially quite strong, persist for 2 minutes—in some cases the pink color faded out entirely in less than 40 seconds. The remaining 14 tests were indistinguishable—in none of the 7 beverages could the sample containing the 0.01% of diethylphthalate be differentiated from the sample of the same beverage containing none of the ester.

SPECIAL COMPARATIVE TESTS ON BEVERAGES.

Owing to the unsatisfactory results obtained by the Calvert method on beverages some additional tests were made. The same sample of sweet wine employed in previous tests was used.

Tests were made for diethylphthalate by our method and by Calvert's method on samples prepared as described in the following table.

TABLE V.—FINAL RESULT.

Sample marked.	Wine. Cc.	Water. Cc.	39-C alcohol. Cc.	Diethylphthal- ate content. %	Pet. ether. Cc.	H. & H. method.	Calvert method.
A	5	5	0.00	None	5	(—)	(—)
B	5	5	0.05	0.01	5	(+)	(—)
C	5	5	0.50	0.1	5	(+) Intense	(+) Faint and very fugitive

It will be noted that it was possible to detect 0.01% of diethylphthalate with absolute certainty by the Handy-Hoyt method on a 5-cc. sample of wine which was subjected to one extraction only with 5 cc. of petroleum ether. On an identical sample the Calvert method failed to detect any diethylphthalate, and with Sample C containing 10 times as much diethylphthalate as B it gave only a faint and very fugitive test.

Recommendations to distil a sample suspected of containing diethylphthalate and apply the test to the distillate are occasionally found. Our own experiments have proved that diethylphthalate can be detected in samples of suitable size taken from any portion of the distillate of a 1% solution of the ester in alcohol (*i. e.*, 39-C alcohol). The amount of ester which distils over from a 1% solution is very small, however, compared to what remains in the flask (our experiments indicate that not over $\frac{1}{25}$ of the ester present distils over); hence we anticipated that it would be difficult to detect the ester in an alcoholic distillate from a beverage containing only a very small amount of the ester. A test was made accordingly.

To 30 cc. of gin was added 0.3 cc. of 39-C alcohol, thus giving a product containing 0.01% of diethylphthalate. A 5-cc. portion of this sample, diluted with 5 cc. H₂O, was extracted once with 5 cc. petroleum ether and the petroleum ether extract tested for diethylphthalate in the usual manner by the Handy-Hoyt method. An unquestionably positive test resulted.

The remaining 25 cc. of the sample were distilled as rapidly as possible with a hot flame and a distillate of 12.5 cc. was collected. This entire distillate was

tested for diethylphthalate by the Handy-Hoyt method. The result was such a faint test as to be doubtfully positive, while the extracted sample of $\frac{1}{5}$ the size gave an unmistakably strong positive test. A 2.5-cc. portion of the residue in the distilling flask was tested without extraction and gave a positive test though obscured by the reddish brown coloration produced by the saccharine matter present. This series of tests shows that much more reliable tests, and on smaller samples, are obtained by extraction instead of distillation of samples whose diethylphthalate content is very small.

GENERAL CONCLUSIONS IN REGARD TO THE THREE DIETHYLPHTHALATE DETECTION TESTS EXAMINED.*

The Calvert test is a very rapid and convenient test which to us appears to be admirably adapted to the detection of diethylphthalate in samples of commercial alcohol suspected to contain it. The Calvert test does not give the troublesome blanks on such samples, which are often given by the other two methods. It should be borne in mind, however, that by the Calvert test saccharin will give a result indistinguishable in intensity and permanency from that obtained with a phthalic acid derivative. In our experience the Calvert test lacks both delicacy and permanency for the detection of small amounts, *i. e.*, such as 0.01%, of diethylphthalate in miscellaneous beverages.

By either the Andrew or the Handy-Hoyt method diethylphthalate can be positively detected on a 5-cc. sample of an alcoholic beverage containing 0.01% by volume of the ester provided the sample is subjected to the simple process of a single extraction with a small volume of petroleum ether and the test applied to the extract. We recognize that this extraction does not remove all of the diethylphthalate present in the sample, but either test is of sufficient delicacy to detect the fraction of ester in the extract. The intensity of the test so obtained persists with no appreciable diminution for several weeks.

Both the Andrew and the Handy-Hoyt methods have their advantages and disadvantages and both give the same satisfactory results if their specific directions are carefully followed. The Andrew method is more rapid and convenient, but requires more personal attention during the evaporation periods.

The Handy-Hoyt method is somewhat longer, involves the use of a 160° C. oil-bath, but requires on the whole less personal attention.

In applying either the Andrew or the Handy-Hoyt method to unknown samples the appearance of the final test solutions should be noted when fresh and again after 24 and 48 hours. A yellowish green fluorescence which persists with undiminished intensity for 48 hours is positive proof of a phthalic acid derivative in the sample. The time element involved in correctly interpreting the results is the principal drawback of the fluorescein-type tests.

IV. ADDITIONAL PROPERTIES OF DIETHYLPHTHALATE.

(A) DETECTION OF DIETHYLPHTHALATE IN THE DISTILLATE FROM 39-C ALCOHOL (*i. e.*, A 1% SOLUTION OF THE ESTER).

Five hundred cc. of a commercial sample of 39-C alcohol were distilled in a 750-cc. distilling flask, using an electric flask heater at a constant heat. The dis-

* It should be emphasized that in our experience the sense of taste applied to a few drops of an unknown alcoholic liquid is capable of detecting diethylphthalate when present to the extent of 0.1%, in the absence of other bitter principles.

tillate was collected in 10–50-cc. portions and distillation was continued until no more distillate issued from the condenser. The bulk of the denaturant remained in the flask but the last fraction of the distillate amounting to 42 cc. contained sufficient diethylphthalate to reveal its presence by taste. A number of fluorescein tests for diethylphthalate were made on different portions and different amounts of the distillate, as follows:

Sample and amount tested.	Result.
20 cc., first 50 cc. fraction.....	+, Distinct
20 cc., 5th 50 cc. fraction.....	+, Distinct
1 cc., 10th (last) fraction.....	+, Distinct
10 cc., made up of 1 cc. each from the 10 fractions.....	+, Distinct
40 cc., made up of 5 cc. each from fractions 1 to 8 (excluding the last 100 cc. of distillate).....	+++ , Intense

The above tests show conclusively that in spite of the great difference in the boiling points of alcohol and diethylphthalate traces of the ester distil over with even the first fractions of distillate of the 1% solution, *i. e.*, 39-C alcohol. Even though the last fifth of the distillate is rejected the ester will be found in sufficient amount in the remainder of the distillate to give an intense fluorescein test provided a reasonably large amount, *e. g.*, 10–20 cc. of sample is used for the test.

(B) SOLUBILITY OF DIETHYLPHTHALATE IN WATER.

Five cc. of the ester were violently shaken for $\frac{1}{2}$ hour in a shaking machine with exactly 500 cc. of distilled water at 20° C. The solution was allowed to settle and was then filtered. This saturated aqueous solution had an intensely bitter taste. Determination of the ester content by semi-quantitative methods indicated that diethylphthalate is soluble in distilled water at 20° C. to the extent of 0.08–0.10 Gm. per 100 cc.

(C) EFFECT OF DILUTION OF COMMERCIAL 39-B AND 39-C ALCOHOLS WITH WATER.

(1) 39-B ALCOHOL (2.5 PARTS DIETHYLPHTHALATE, BY VOLUME, TO 100 PARTS ALCOHOL, BY VOLUME).

Distilled water was added from a graduated pipette to a known volume of 39-B alcohol until a faint permanent turbidity resulted at room temperature. It was found that this occurred when 2.1 volumes of water had been added to 1 vol. of 39-B. It was noted, however, that on standing the mixture became much more turbid—almost milky in appearance. This was found to be due to a change in temperature—the dilution of the alcohol evolving considerable heat, and the solubility of diethylphthalate in alcohol water mixtures is a function of the temperature, as was pointed out by Lyons.

The following facts were observed:

One vol. of 39-B alcohol at 20° C., diluted with 2.0 volumes of distilled water at 20° C., gives a mixture whose temperature is 27° C. (immediately after mixing) and which is clear at that temperature but becomes slightly turbid on cooling to 20° C.

(2) 39-C ALCOHOL (1 PART DIETHYLPHTHALATE, BY VOLUME, TO 100 PARTS ALCOHOL, BY VOLUME).

Dilution of this alcohol with amounts of water up to 20 times the volume of the alcohol do not at any of these dilutions produce a solution having a distinct

turbidity at ordinary room temperature. (The solubility of diethylphthalate in water alone being approximately $1/10$ of 1%, a dilution of 39-C alcohol with 10 vols. of water would provide enough aqueous solvent for the complete solubility of the ester present. When diluted with less than 10 vols. of water there is sufficient alcohol present to keep the small amount of ester in solution.)

V. PRELIMINARY RESULTS ON GERMICIDAL, PHARMACOLOGICAL AND TOXICOLOGICAL PROPERTIES OF DIETHYLPHTHALATE.

(A) THE PHENOL COEFFICIENT METHOD OF THE U. S. DEPT. OF PUBLIC HEALTH.

This method (*Hygienic Laboratory Bulletin*, No. 82, pub. 1912) was used, with modification as to the organism employed.

Bacillus pyocyaneus, which we have found by a number of previous phenol coefficient tests to give substantially the same results as *B. typhosus*, was used in this series of tests.

Conditions of test:

Culture used—24-hour broth culture of *B. pyocyaneus*, filtered. (Carried over daily, in broth, for 4 days.)

Amount of culture used—0.1 cc. to 5 cc. of disinfectant solution.

Temperature of medication—20° C.

Time of medication—2½, 5, 10 and 15 minutes.

Subculture—1 loopful (loop made 4 mm. in diameter, of 23 ga. Pt. wire) to 10 cc. extract broth, reaction +0.5.

(N. B.: This reaction is most favorable for the growth of *B. pyocyaneus*.)

Period of incubation—48 hours at 37° C.

Since diethylphthalate is so slightly soluble in water, and is not of course in its concentrated form miscible with culture media it was necessary also to make tests on solutions of diethylphthalate in alcohol. Mixtures representing 39-B and 39-C alcohols were made up, using cologne spirits. In the disinfectant tests the cologne spirits employed were also tested, in the same dilutions.

RESULTS.

No.	Sample.	Time.			
		2½.	5.	10.	15.
1	C. P. phenol 1-80
2	C. P. phenol 1-100	+	+	+	+
3	Saturated aqueous solution of diethylphthalate	+	+	+	+
4	Diethylphthalate, pure ester	+	+	+	...*
5	Cologne spirits, undiluted
6	Cologne spirits, 1% diethylphthalate (<i>i. e.</i> , 39-C alcohol)
7	Cologne spirits, 2.5% diethylphthalate (<i>i. e.</i> , 39-B alcohol)
8	Cologne spirits diluted with twice its volume of sterile distilled water	+	+
9	39-C alcohol—dil. 1 to 2, like Sample 8
10	39-B alcohol—dil. 1 to 2, like Sample 8

* Culture and ester not miscible. Probably in making this transfer a loopful of ester free from bacteria was added to the subculture.

In the above table under time a + sign indicates growth of culture and the ... sign indicates no growth.

CONCLUSION.

The foregoing table shows, Tests 8, 9 and 10, that diethylphthalate has a restraining influence on the growth of bacteria, but that the disinfecting power of the ester is comparatively small.

(B) PHARMACOLOGY AND TOXICOLOGY.

Diethylphthalate was administered, per ora, to an adult cat. Four drops of the pure ester, equivalent to about 75 milligrams per kilo of body weight, were employed. This dose was twice repeated at intervals of 48 hours. No appreciable physiological disturbance was noted, the only effects being to somewhat diminish the appetite and increase the sluggishness of the animal, which became, however, entirely normal within 3-4 days after the last dose was administered.

VI. REVIEW OF THE LITERATURE AND MARKET CONDITIONS IN REGARD TO DIETHYLPHTHALATE.

With the exception of the scientific articles on the detection of diethylphthalate already mentioned, little data have appeared in the literature during the past year in regard to this chemical.

In the *Pharmazeutische Zeitung* for Jan. 31, 1923, p. 86, is a brief official notice concerning diethylphthalate by Steinkopff (9) of the German Alcohol Monopoly Office. This notice, effective in January 1923, reduces the quantity of diethylphthalate used as a denaturing agent in alcohol intended for use in a variety of manufacturing processes, including perfumes, cosmetics, and scientific preparations and chemical investigations of all kinds from 2 volumes of the ester per 100 volumes of spirits to 1 volume. The official notice further gives rather liberal specifications (*i. e.*, color, odor, specific gravity, boiling point and saponification number) to which the ester for this purpose must conform.

Dr. J. M. Doran (10), speaking before the April 1923 meeting of the American Manufacturers of Toilet Articles, discusses the use of 39-C alcohol and diethylphthalate as follows:

"On August 2, 1922, Formula 39-C was authorized. The authorization of this formula was a direct result of the efforts of your Industrial Alcohol Committee in coöperation with the Department and I am happy to say that its procurement and use have been uniformly satisfactory. At least no complaints have reached the Department, and further, from the restricted character of the applicants who can qualify to use this formula, I anticipate no trouble arising from its use. The question of the quality of the denaturant, diethylphthalate, which was of great concern to us a year ago, seems to be working itself out along normal lines. As many of us anticipated at that time, the first rush of manufacturing in this country had produced some inferior products which have been practically eliminated by time and experience and the normal action of competition."

Subsequently Dr. Doran, at this same meeting, confirmed a statement by Mr. Harrison that while no exact figures were available showing the relative amounts of pure alcohol and the denatured alcohols 39-B and 39-C used by manufacturers, these two denatured alcohols were being very generally used with good satisfaction.

During the past year the quality of the diethylphthalate on the market has improved, *i. e.*, with regard to objectionable odor and color. The price has dropped from about 85-90 cents to 55-60 cents per pound, due both to a drop in the price of the raw material (phthalic anhydride) and to a lessened demand, owing to the restrictions placed on the use of alcohol No. 39-B as a rubbing alcohol.

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LABORATORIES OF LARKIN CO., INC.,
BUFFALO, N. Y.

ZINC HYPOCHLORITE.

BY J. A. W. LUCK.

The preparation of solid zinc hypochlorite was attempted by Lunge and Landolt.¹ Their procedure consisted in passing dried chlorine gas over freshly prepared and dried zinc hydroxide. They also attempted to prepare magnesium hypochlorite in a similar manner. However, their results were negative in both cases.

In the preparation of calcium hypochlorite it has been found that the presence of water is a necessary condition, the degree of chlorination varying with the original water content of the calcium hydroxide. Calcium hypochlorite, having an available chlorine content of 76.62%, has been described by Hofmann and Ritter.² This material was furnished them by the Griesheim-Elektron Company and was prepared according to the specifications of a German patent.³ The manufacture of pure calcium hypochlorite $\text{Ca}(\text{OCl})_2$ is described in a later patent.⁴ The specifications of this patent state that chlorine gas is passed through milk of lime, the suspended calcium hydroxide dissolves and a precipitate forms which redissolves after continued passage of chlorine gas through the solution. Upon the addition of a saturated solution of calcium chloride, pure calcium hypochlorite crystallizes from this solution.

Solutions of zinc hypochlorite are described in various books.⁵ These solutions were prepared by passing chlorine gas through suspensions of zinc hydroxide or zinc oxide in water; the suspended material dissolves forming zinc hypochlorite, chloride and chlorate. In some of these experiments a solid residue remained after the chlorine gas ceased to be absorbed. It seems that none of these investigators examined this residue.

While analyzing a number of zinc hypochlorite solutions, the writer found that solutions containing some of this suspended residue had a larger available chlorine content than clear solutions. This led to an examination of the solid material.