

of proper filters the ultraviolet may be broken up into narrow monochromatic bands and the absorption of the various liquids for each wave-length studied. Such technic, while less refined, is much less expensive and elaborate than that required when using spectrophotometers, and would probably be satisfactory for studying certain aspects of the relation between ultraviolet absorption and chemical constitution.

DETERMINATION OF PHENOLPHTHALEIN IN PHARMACEUTICAL MINERAL OIL EMULSIONS.*

BY J. A. SERRALLACH AND R. J. OWEN.

Phenolphthalein in various combinations has been used for many years as a laxative in the treatment of constipation. One of the present most popular forms of administering it is as added to mineral oil emulsions in concentrations of from 0.3 to 1.4 per cent. A diligent search of the literature has revealed no method by which the phenolphthalein content in such preparations can be quickly and accurately determined.

Warren (1) has published analyses of several commercial mineral oil emulsions, one of which contained phenolphthalein. He determined roughly the phenolphthalein content in it. The procedure consisted in (a) adding ammonia and alcohol to the emulsion, (b) extracting the oil with ether and petrol-benzene, (c) evaporating the aqueous solution to dryness, (d) extracting the residue with cold water, (e) filtering to separate from emulsifiers insoluble in cold water, (f) precipitating the rest of the emulsifiers with alcohol, and (g) evaporating the alcoholic filtrate to dryness. This residue was called "sodium benzoate, soluble saccharin or phenolphthalein." It was recognized that through this procedure part of the phenolphthalein had gone into the ether-petrolbenzene solvent, due to the fact that ammonia does not hold the phenolphthalein entirely in the aqueous alcoholic solution. This method has two further disadvantages. Through the various steps in the analysis some of the phenolphthalein is lost and, as the concentration of the phenolphthalein is very low in the emulsion and fairly small quantities only can be taken for analysis, the error is considerable. Furthermore, the time required for such a determination is long.

The other methods which have been proposed for determining phenolphthalein are intended for pharmaceutical preparations not containing oil. Two of them are volumetric (2), (3). The others are gravimetric (3), (4). All of them take advantage of the solubility of phenolphthalein in either sodium hydroxide or organic solvents and were worked out for dry preparations (for instance, pills) containing no oil. In the case of mineral oil emulsions it is possible to follow somewhat any one of these methods by first breaking the emulsion by the addition of acid and heat treatment to hydrolyze the emulsifier, then neutralizing the acid, evaporating the aqueous part to dryness and extracting the phenolphthalein. Such a procedure is inaccurate and time consuming due to the numerous steps required. Also the

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extract that is finally weighed contains partly or completely the preservatives (salicylic acid, benzoate, etc.) and flavoring ingredients, etc., present in the original emulsion.

A colorimetric method has been developed for determination of phenolphthalein in oil emulsions which is quick and accurate and which might be used to advantage for controlling the phenolphthalein content of such preparations.

The procedure is as follows:

Ten grams of emulsion are weighed accurately and diluted in a volumetric flask to exactly 100 cc. with distilled water. Two cc. of this solution are then diluted to 25 cc. with alcohol, also accurately in a volumetric flask. A standard solution of phenolphthalein is prepared by dissolving 10 milligrams in 100 cc. of 96% U. S. P. Alcohol. One-half cc. of each of the alcoholic solutions of known and unknown phenolphthalein concentration are accurately measured with a fine, graduated 1-cc. pipette and mixed in two separate 20-cc. portions of $N/100$ NaOH in two 25-cc. Nessler tubes of the same diameter. The tubes are then placed in a colorimeter similar to the ones used with standard p_H determination sets. The arrangement in the colorimeter is as follows:

CONTENTS OF TUBES.

<i>Front row</i>	<i>a.</i> Unknown solution of phenolphthalein	<i>b.</i> Known solution of phenolphthalein
<i>Back row</i>	<i>c.</i> Distilled water	<i>d.</i> 20 cc. distilled water + 1 cc. of unknown solution.

The colors of the known and unknown phenolphthalein solutions are then brought to match; in this case the difference is not large, by diluting the stronger of them with a few cc. of $N/100$ NaOH and stirring with a glass rod. If the color difference is considerable, however, new mixtures of the unknown solution with the $N/100$ NaOH solution are made with more than $1/2$ cc. or less of the alcoholic solution, depending upon whether the solution under examination is stronger or weaker. The solution that is more pink is then diluted as above with $N/100$ NaOH to bring both solutions to match exactly in color. If the solutions still cannot be brought to match by diluting the stronger one with $N/100$ NaOH, a new, more diluted solution or stronger is made from the unknown solution, and the procedure repeated as above described. The amount of phenolphthalein present can then be calculated from the dilutions.

The table below shows results obtained with synthetic mixtures prepared by making mineral oil emulsions and adding the phenolphthalein in a manner similar to that used by manufacturing concerns.

TABLE I.

Phenolphthalein added.	Phenolphthalein found.
1.32%	1.36%
1.32	1.34
0.48	0.46
0.48	0.45

The phenolphthalein content of a few mineral oil emulsions on the market was also determined by this method. The results were:

Commercial sample.*	Amount claimed.	Amount found.
1	0.48 per cent	0.50 per cent
2	0.32	0.28
3	?	0.32
4	1.45	1.45

* Preparations 2, 3, 4 contain agar-agar as emulsifiers, Preparation 1 contains the mucilage of the seaweed Irish Moss.

The comparisons should always be made in fresh solutions, because the color of the diluted alkaline phenolphthalein solutions slowly fades through the action of CO₂ from the atmosphere.

LITERATURE CITED.

- (1) Warren, "Reports of the Chem. Lab. of the Am. Med. Assoc.," 17, 18, 20 (1924-1925).
- (2) Zotier, *Bull. soc. chim.* [4], 7 (1910), 993-995.
- (3) Kollo, *Apoth. Ztg.*, 24, 283 (four different methods), *Pharm. Praxis*, 7 (1908), 341-344.
- (4) Rosenberger, *Chem.-Ztg.*, 54 (1930), 345.

THE SAMPLING OF OPIUM.

BY FREDERIC ROSENGARTEN.

The Testing or "Assay" of Opium is a subject that has received and is receiving considerable attention. From time to time many discussions on this subject have taken place and more are impending. As little or nothing has been said about the practical aspects of sampling the drug, the writer's experience may prove of some service to those interested.

No matter how consistent the method of testing may be, results cannot be correct if the sample under observation does not truly represent the lot of opium in question. Not only does every piece of opium vary from all the other pieces in a shipment, but each piece varies more or less in itself, from circumference to its center. This is particularly true of opium originating in Mediterranean countries. Such descriptions as Persian Opium, which are reputed to be packed for shipment from bulk that has been more or less thoroughly mixed, are more uniform.

The writer observed the collection of opium, during the harvesting season, in Asia Minor some thirty years ago, and from personal observation it gives him pleasure to confirm the procedure in connection with the collection of the juice, as described in "Flückiger's Pharmacographia," published in London, 1874. He should add that local merchants, as well as shippers, are skilled in the "grading" of opium, a process not based on any scientific method, but upon the appearance and consistency of the drug. As reliable shippers usually "grade" their shipments so that every chest in a shipment contains the same proportion of good, medium, indifferent and poor pieces, the sampling of such uniform shipments is much simplified. On the other hand when shipments are packed in a haphazard manner it may become necessary to dry and powder the entire shipment, in order to obtain a representative sample after the powdered drug has been thoroughly and uniformly mixed in a mechanical mixer. Notice must be taken of the fact that if opium is abused during the drying process the percentage of morphine will be diminished. The drug should not be overheated. The most desirable method of drying is to employ a vacuum dryer.