

## GENERAL CONCLUSION.

The aluminum-stannous-chloride-hydrochloric-acid reaction has very good possibilities as a substitute for the zinc-sulphuric acid reaction in the Gutzeit test in that many difficulties met with in arsenic-testing by the present zinc-procedure are eliminated.

The Dutch Pharmacopœia V (5) has a Gutzeit arsenic-testing procedure in which is directed a method somewhat similar to that developed in this work. However, 0.2 Gm. of aluminum or 0.5 Gm. of zinc and 3 cc. of a one per cent acid-stannous-chloride solution are used in the Dutch Pharmacopœia. This method is claimed to detect one micro-milligram of arsenic (As). A much smaller amount (0.4 micro-milligram) is detectable by the method herein dealt with. It will be noted that the amount of stannous chloride used by the Dutch Pharmacopœia is much less in proportion to that employed in the method recommended. Because of the insufficient amount of stannous chloride used, the Dutch Pharmacopœial method, although using aluminum, is not likely to be as delicate as the method of procedure herein described.

## BIBLIOGRAPHY.

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- (2) Treadwell Hall, Analytical Chemistry, Vol. II, 7th Edition.
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- (4) C. R. Sanger and O. F. Black, *Journal of the Society of Chemical Industry*, 36 (1907), 115-123.
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## THE ULTRAVIOLET TRANSMISSION OF LIQUIDS.

BY ELLERY H. HARVEY.

*(Concluded from the November 1930, number.)*

## QUANTITATIVE DISTRIBUTION OF THE LIGHT.

Range Å.	Per cent total radiation.
3020 to 3600	2.0
3600 to 4800	18.5
4800 to 6000	9.3
6000 to 14000	16.5
14000 to 42000	22.1
42000 to 120000	31.6

Since the wave-lengths of the source of light approximate rather closely those received from the sun, and the intensity of the former is 4700 foot-candles while a bright Chicago day between the hours of 12 noon and 2 P.M. registers slightly in excess of 4000 foot-candles, the results reported may be considered somewhat comparable to sunlight exposure.

The basis of calculation is the number of milligrams of oxalic acid decomposed in two hours irradiation, using distilled water (or equally transparent media) in the quartz cell as the screen. All determinations gave the same value, *i. e.*, 140.4 mg. Water being transparent to ultraviolet of this wave-length, the value of 140.4 mg. was taken as 100% transmission and all results obtained calculated to

this base line. Obviously the absorbency of any liquid screen is the per cent transmission subtracted from 100.

PART I. THE ULTRAVIOLET TRANSMISSION OF ESSENTIAL OILS.

Application of the method just outlined has been made in a study of the ultraviolet transmission of forty typical essential oils, a subject of very considerable interest because of its bearing on the larger practical problem of the photochemical decomposition of many pharmaceutical products improperly stored in glass. Significance of the data has been increased by using oils of known quality. Where no mention is made of this point in Column 2 of Table I, the oil was of the highest purity commercially available. The effect produced by the absorption of ultraviolet light on the physical properties is being determined and will be reported later.

TABLE I—ULTRAVIOLET TRANSMISSION OF ESSENTIAL OILS.

3-mm. layer of oil acting as screen to ultraviolet transmission.	Quality of oil used.	Milli-grams of oxalic acid decomposed in two hours.	Percentage transmission based on water as 100%.	3-mm. layer of oil acting as screen to ultraviolet transmission.	Quality of oil used.	Milli-grams of oxalic acid decomposed in two hours.	Percentage transmission based on water as 100%.
Bergamot		0.0	0.0	Fennel	U. S. P. IX	83.1	59.2
Cinnamon	Ceylon	1.2	0.9	Dillseed		83.1	59.2
Rose Geranium	Old sample	2.5	1.8	Tansy		83.1	59.2
Curcuma		3.1	2.2	Marjoram	Sweet cultivated	86.3	61.4
Pimento	U. S. P. IX	3.7	2.7	Juniper berries	U. S. P. IX	97.0	69.2
Rue		5.0	3.6	Coriander	U. S. P.	107.1	76.3
Clove	U. S. P. IX	5.0	3.6	Peppermint	U. S. P. IX	108.3	77.2
Lemongrass		6.3	4.5	Thyme	White	110.2	78.5
Estragon		11.9	8.5	Sage	Dalmatian	113.4	80.8
Limes	Handpressed	18.9	13.5	Cedarwood		113.4	80.8
Mace		19.5	13.9	Pepper, black		118.4	84.3
Celery seed		21.4	15.3	Anise	U. S. P. IX	119.7	85.3
Orange	U. S. P. IX	32.7	23.3	Lavender	U. S. P. IX	124.1	88.4
Spearmint	U. S. P.	39.0	27.8	Rosemary	U. S. P. IX	126.0	89.8
Caraway	U. S. P. IX	42.2	30.1	Nutmeg	U. S. P.	126.6	90.2
Citronella		47.8	34.1	Wintergreen	U. S. P. VIII	127.2	90.6
Lemon	U. S. P. IX	49.7	35.4	Camphor		129.7	92.4
Parsley		51.0	36.4	Cajeput	U. S. P. X	137.3	97.8
Eucalyptus	U. S. P. IX	51.0	36.4	Turpentine	Spirits	139.2	99.2
Limes	Distilled	52.3	41.7	Water	Distilled	140.4	100.0
Ginger	Pure	72.4	51.6				

DISCUSSION.

Assuming the application of the Grotthus generalization that only those rays of light which are absorbed produce chemical action, the results obtained indicate the widest possible variation with respect to possible photochemical changes among members of this group of naturally occurring substances. Beginning with bergamot, which absorbed the maximum and would therefore be subject to the greatest changes induced by ultraviolet, we have a continuing and rather regular decrease in absorption down to turpentine which absorbed practically no ultraviolet. How well this agrees with practical experience cannot be determined from

a perusal of the literature since quantitative measurements of this sort have not been recorded.

The application of this information is obvious. Adequacy of storage conditions must be in proportion to the known relative susceptibility of the oil to absorb ultraviolet, if the chemical changes produced by the latter are to be avoided. None of the oils possessing complete immunity, it would be necessary to store in glass, if the latter is to be used, known to be opaque to the passage of ultraviolet light. Of bottles found in the ordinary drug store, the writer<sup>1</sup> found that the colorless and blue glasses afforded but little protection, whereas dark brown glass bottles were quite opaque. The importance of the subject would justify a suitable statement in the Pharmacopœia to the end that the care taken to secure high quality would not be nullified by improper containers.

#### OTHER APPLICATIONS OF THE DATA.

The possible use of the method in connection with identification and evaluation through the development of "constants," so important in the field of organic analysis, has occurred to us. Until the effect of such variables as constitution, age, variety, geographical distribution, climatic and soil conditions and others, has been determined, discussion must be postponed. We are at this time merely pointing out the problem.

Based on the assumption that the principal constituent exerts the greatest influence on the ultraviolet transmission of the oil in which it is found, a brief excursion has been made into this field, using aromatic chemical constituents made by the same manufacturers from whom most of the oils were purchased.

TABLE II.—CALCULATED EFFECT THE PRINCIPAL CONSTITUENT HAS IN AFFECTING THE ULTRAVIOLET TRANSMISSION OF AN OIL.

Essential oil.	Ultraviolet transmission of the oil, %.	% of principal constituent normally present.	Ultraviolet transmission of principal constituent, %.	Calc. % of principal constituent.
Anise	85.3	80-90 anethole	96.0	12.0
Caraway	30.1	50-60 carvol	45.2	34.0
Cinnamon	0.9	65-80 cinnamaldehyde	5.9	85.0
Citronella	34.1	50-80 citronellal	95.1	65.0
Clove	3.6	80-95 eugenol	66.4	94.6
Eucalyptus	36.4	55-80 cineol	95.6	62.0
Fennel	59.2	50-70 anethole	96.0	39.0
Juniper berries	69.2	35 pinene	96.0	28.0
Lavender	76.3	30-55 linalyl acetate	96.4	21.0
Lemon	35.4	76-90 limonene	96.0	63.0
Lemongrass	4.5	68-85 citral	24.3	82.0
Orange	23.3	90 limonene	96.0	76.0
Wintergreen	90.6	98-99 methyl salicylate	90.6	99.0

The agreement between the figures in Column 3 and Column 5 is no better than expected keeping in mind that at least three important variables are involved:

1. Constituents other than the principal ingredient may absorb ultraviolet.
2. The oil examined may not have had the amount of principal constituent normally present.

<sup>1</sup> Harvey, *Am. J. Pharm.*, 100 (1928), 523-528.

3. The principal constituent may not have been of the same purity in the oil as that examined.

PART 2. THE ULTRAVIOLET TRANSMISSION OF FATTY OILS.

Two common examples of the part played by ultraviolet light in inducing changes in fatty oils are those collectively known as rancidity, in which, while being imperfectly understood, the accelerating influence of light is generally acknowledged, and secondly, those oxidations and polymerizations occurring in drying oils which form the basis of the paint industry. In so far as ultraviolet fairly comparable to that found in sunlight is absorbed and would tend to play a part in inducing chemical and physical changes, the data below in Table III has a direct practical value. It is recognized of course that while ultraviolet may be absorbed, it does not follow that it necessarily will produce chemical action.

TABLE III.—ULTRAVIOLET TRANSMISSION OF FATTY OILS.

3-mm. layer of oil acting as screen to ultraviolet transmission.	Quality of oil used.	Milli-grams of oxalic acid decomposed in two hours.	Percentage of ultraviolet transmitted based on water as 100%.	3-mm. layer of oil acting as screen to ultraviolet transmission.	Quality of oil used.	Milli-grams of oxalic acid decomposed in two hours.	Percentage of ultraviolet transmitted based on water as 100%.
Linseed	Boiled	3.7	2.7	Sperm		97.0	69.1
Whale		8.1	5.8	Cottonseed		126.6	90.2
Linseed	Raw	10.7	7.7	Corn		128.5	91.6
Rapeseed		15.1	10.8	Almond	U. S. P. IX	130.4	92.7
Chinawood		39.0	27.8	Olive	U. S. P. IX	135.4	96.5
Codliver	U. S. P. IX	57.3	40.9	Sesame	U. S. P. IX	136.0	96.9
Lard oil		77.4	55.2	Peanut		137.3	97.8
Soyabean	Old sample	78.1	55.7	Castor	U. S. P. X	138.6	98.8
Neatsfoot		96.3	68.6				

While the method is non-selective and gives the total effect of all constituents on ultraviolet absorption, it cannot help being noticed that unsaturation has a tendency to group the oils roughly in the table where absorption is most marked.

PART 3. THE ULTRAVIOLET TRANSMISSION OF CRUDE PETROLEUM OILS.

A set of typical crude oils was examined for ultraviolet transmission after dilution with carbon tetrachloride, the original oils being too dense. A somewhat greater dilution would have been desirable. These oils represent every important producing area, and data covering their physical characteristics have been prepared for publication.

TABLE IV.—ULTRAVIOLET TRANSMISSION OF CRUDE OILS.

3-mm. layer consisting of 1 cc. of crude oil added to 50 cc. CCl <sub>4</sub> .	Milli-gram of oxalic acid decomposed in two hours.	Percentage of ultraviolet transmitted based on carbon tetrachloride as 100%.	3-mm. layer consisting of 1 cc. of crude oil added to 50 cc. CCl <sub>4</sub> .	Milli-grams of oxalic acid decomposed in two hours.	Percentage of ultraviolet transmitted based on carbon tetrachloride as 100%.
Kansas, Butler County, Augusta Field	0.0	0.0	Oklahoma, Creek County, Cushing Field	1.3	0.9
California, Los Angeles County, Santa Fe Springs Field	0.0	0.0	Louisiana, Acadia County, Jennings Field	3.7	2.6
			Russia, Baku	7.5	5.3

Wyoming, Hot Springs County, H a m i l t o n Dome Field	0.0	0.0	Oklahoma, Carter County, Healdton Field	9.4	6.7
California, Kern County, Buena Vista Field	0.0	0.0	Wyoming, Hot Springs County, Grass Creek Field	12.6	8.8
Louisiana, Caddo County, Caddo Field	0.0	0.0	West Virginia, Lincoln County, Freeman Dis- trict	21.4	15.2
Kentucky, Lee and Estell Counties, Pryce Station	0.0	0.0	Montana, Cat Creek	24.5	17.5
Ohio, Aggerton Station	0.0	0.0	Pennsylvania, Washington County	89.4	63.7
Texas, Limestone County, Mexia Field	0.0	0.0			

#### PART 4. ULTRAVIOLET TRANSMISSION OF MISCELLANEOUS LIQUID CHEMICALS.

A group of miscellaneous liquids have been included in Table V. The high absorption of ultraviolet by sulphur monochloride confirms previous work by the writer<sup>1</sup> where it was found that sunlight produced a generous evolution of hydrochloric acid.

TABLE V.—ULTRAVIOLET TRANSMISSION OF VARIOUS LIQUIDS.

Chemical.	Purity.	Percentage transmission based on water as 100%.
Acetic acid	Glacial	95.1
Alcohol, amyl	C.P.	97.6
Alcohol, ethyl	95%	94.5
Alcohol, methyl	C.P.	95.1
Carbon tetrachloride	Pure	100.0
Chloroform	U. S. P. X	95.6
Cresol	U. S. P. X	39.9
Creosote, beechwood	U. S. P. X	46.3
Ethylene glycol	Eastman practical	52.0
Ethyl lactate	Eastman practical	96.0
Glycerin	U. S. P. X	99.2
Lactic acid	U. S. P. 85%	96.0
Nitrobenzene	Commercial	3.2
Petrolatum, liquid	U. S. P. X	100.0
Sulphur monochloride	Merck	1.8

#### SUMMARY.

The historical development of the method for measuring ultraviolet by the decomposition of oxalic acid catalyzed with uranium salts has been traced. The technic has been modified to measure the absorption or transmission of liquids. Such a method has several advantages: it is quantitative, measures only the effect of the ultraviolet, is unselective and is practically unaffected by ordinary temperatures. Since the quality of the ultraviolet used is somewhat comparable to sunlight and assuming in general that the converse of the Grotthus generalization is true, the data has a certain practical significance in connection with such problems as the proper storage of substances of pharmaceutical interest.

The method has been applied to a group of essential, fatty and crude oils and to several liquid chemicals. Of the former the possibility of approximating the per cent of the principal constituent has been briefly discussed. By the use

<sup>1</sup> Harvey, Ph.D. Thesis, University of Wisconsin, 1926.

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.

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## 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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\* Contribution from the Research Laboratory of Applied Chemistry, Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Mass.