AN ULTRAVIOLET SPECTROPHOTOMETRIC QUALITY AND STABILITY CRITERION FOR MEDICINAL LIQUID PARAFFIN

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Medicinal liquid paraffin is required to be water white, odourless, tasteless, and free from biologically harmful impurities. Its viscosity and specific gravity are specified by various Pharmacopœias and are accessible to direct measurement. As far as carbonisable constituents are concerned the British Pharmacopœia, 1948, stipulates an acid test by which materials pass with "acid numbers" of less than 2·5 Red, 6·5 Yellow. A detailed study of the physical meaning of the B.P. acid test[1] shows that the ultraviolet absorption spectrum of medicinal liquid paraffin is an objective measure of its quality and that a stability criterion can be based on the spectrophotometric data in the wavelength region between 2400 Å and 2800 Å. A plot of the absorption intensity against wavelength exhibits for most liquid paraffins a minimum, if it is a stable oil, in the neighbourhood of 2490 Å, with a maximum in the neighbourhood of 2710 Å, and with a subsidiary maximum at about 2780 Å (Fig. 1). If the ratio of the absorption intensities at the maximum at 2710 Å and at the minimum at 2490 Å is above 2·0 the material is stable, that is, it does not develop any odour or taste and it does not suffer discoloration on exposure to daylight for several months (Table I). For a good quality medicinal liquid paraffin the absorption intensity at 2710 Å should have a value $E_{1\text{ cm.}}^{1\text{ per cent.}} \leqq 0{\cdot}100$. Extremely pure liquid paraffins may have absorption intensities at 2710 Å as low as $E_{1\text{ cm.}}^{1\text{ per cent.}} = 0{\cdot}003$, and in these cases the spectrum has no definite band structure and the material is very stable on exposure to daylight for a period of years. Actually spectra have been taken of very stable liquid paraffins having $E_{1\text{ cm.}}^{1\text{ per cent.}} = 0{\cdot}0005$. On the other hand, for an unstable liquid paraffin (Fig. 2) the position of the minimum is usually displaced towards longer wave lengths between 2500 Å and 2620 Å.

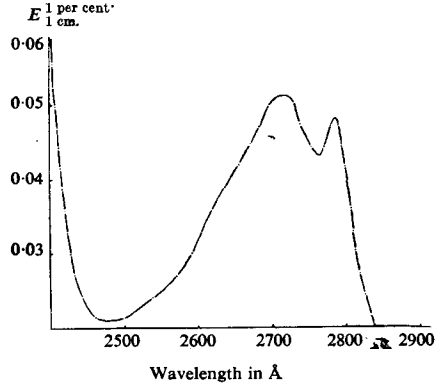

Fig. 1.—Absorption curve of stable sample of liquid paraffin.

It has been found that the results of the B.P. acid test bear no relation to the quality of medicinal liquid paraffin as determined by spectrophotometric evidence (*see* Table II, Group III and IV). In fact a medi-

cinal liquid paraffin of good quality by spectrophotometric evidence may fail the B.P. acid test, while extremely pure liquid paraffin may yield acid numbers varying between 0·9 Red, 2·0 Yellow and 1·7 Red,

TABLE I

COMPARISON OF ABSORPTION SPECTROPHOTOMETRIC AND B.P. ACID TEST DATA OF DIFFERENT STABILITY CLASSES OF MEDICINAL LIQUID PARAFFIN (ORDERED ACCORDING TO THEIR ABSORPTION RATIOS, I.E., GROUP I, THOSE HAVING RATIOS > 2·0, GROUP II, WITH RATIOS BETWEEN 1·8 AND 2·0, GROUP III, WITH RATIOS BETWEEN 1·2 AND 1·8, AND GROUP IV, WITH RATIOS <1·2)

Group	Absorption at Maximum		Absorption at Minimum		Ratio of absorption intensities at maximum and minimum	B.P. acid test		Stability
	$E^{1\text{ per cent.}}_{1\text{ cm.}}$	Å	$E^{1\text{ per cent.}}_{1\text{ cm.}}$	Å		Red	Yellow	
I ...	No band structure, $E^{1\text{ per cent.}}_{1\text{ cm.}}$ = 0·00049 at 2700 Å					0·9	2·7	2 years +
	0·0099	2719	0·0037	2500	2·68			7 months +
	0·0492	2718	0·0209	2492	2·35	2·2	5·9	6 months +
	0·0133	2710	0·0060	2470	2·22	1·2	2·4	6 months +
	0·0557	2714	0·0253	2506	2·20	1·5	3·8	5 months +
	0·0411	2716	0·0189	2492	2·18	1·3	2·9	6 months +
II ...	0·0640	2708	0·0327	2508	1·96	1·2	3·2	2 months
	0·0363	2705	0·0188	2482	1·93	1·0	2·5	5 months (slight trace of odour)
	0·0769	2729	0·0422	2492	1·82	1·5	3·7	10 days
	0·1003	2713	0·0550	2501	1·82	1·3	3·4	2 months
III ...	0·0726	2707	0·0478	2518	1·52	1·1	3·1	21 days
	0·0897	2706	0·0601	2512	1·49	1·1	2·2	14 days
IV ...	0·0704	2735	0·0595	2555	1·18	1·1	2·7	33 days
	0·0954	2717	0·0809	2530	1·18	1·1	3·3	31 days

4·2 Yellow, whereas a very poor liquid paraffin by spectrophotometric evidence (for instance, $E^{1\text{ per cent.}}_{1\text{ cm.}}$ = 0·0494 at 2706 Å and $E^{1\text{ per cent.}}_{1\text{ cm.}}$ 0·0416 at 2607 Å (ratio of absorption intensities: 1·18)) may show the comparatively low acid number of 0·8 Red, 1·7 Yellow. The difficulty with the B.P. acid test appears to be that 96 per cent. sulphuric acid in addition to reacting with the minute quantities of hydroaromatic compounds present in the refined product dehydrogenates naphthene molecules.

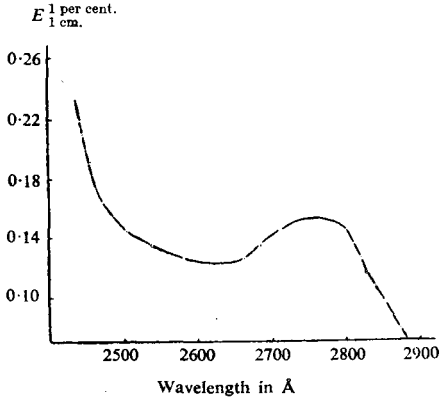

FIG. 2.—Absorption curve of unstable liquid paraffin.

At any rate it has been possible to isolate by chromatographic separation two groups of compounds (A and B) from medicinal liquid paraffin. The Group A compounds show an absorption band at about 2700 Å with an intensity of $E^{1\text{ per cent.}}_{1\text{ cm.}} \sim 15$ (Fig. 3), whereas the Group B com-

pounds have an absorption spectrum with the intensity rapidly decaying at wavelengths above 2400 Å (Fig. 4). The ultraviolet absorption spectrum of medicinal liquid paraffin is the superimposition of the spectra of these two groups of compounds in the proportions in which they are present, on the very weak background absorption of the naphthene-paraffin molecules.

TABLE II

DATA SHOWING THE LACK OF CORRELATION BETWEEN THE ULTRA VIOLET ABSORPTION SPECTROPHOTOMETRIC DATA AND THE B.P. ACID TEST NUMBERS OF MEDICINAL LIQUID PARAFFIN

Group	Absorption at				Ratio of absorption intensities at maximum and minimum	B.P. acid test	
	Maximum		Minimum				
	$E_{1\text{ cm.}}^{1\text{ per cent.}}$	Å	$E_{1\text{ cm.}}^{1\text{ per cent.}}$	Å		Red	Yellow
I	0·0304	2706	0·0094	2480	3·23	1·3	3·3
	0·0334	2700	0·0108	2484	3·10	0·8	2·0
	0·0178	2695	0·0064	2480	2·78	1·0	2·1
	0·00905	2709	0·00339	2485	2·67	2·3	5·6
	0·0993	2715	0·0428	2484	2·32	1·1	3·3
	0·0275	2699	0·0124	2486	2·2	2·0	5·0
	0·0411	2716	0·0189	2492	2·18	1·3	2·9
	0·0291	2700	0·0136	2481	2·14	1·6	4·2
	0·0776	2702	0·0362	2504	2·14	2·8	8·0
	0·0993	2715	0·0468	2487	2·12	1·1	3·3
II	0·0696	2719	0·0357	2476	1·95	2·2	5·9
	0·0351	2700	0·0181	2475	1·94	1·8	3·8
	0·0313	2715	0·0162	2482	1·93	1·6	3·5
	0·0318	2716	0·0164	2497	1·93	0·8	2·3
	0·0363	2689	0·0188	2489	1·93	1·8	4·1
	0·0256	2710	0·0142	2493	1·8	2·3	5·7
III	0·0053	2711	0·0030	2484	1·77	2·3	6·2
	0·0208	2714	0·0121	2508	1·71	1·0	3·1
	0·0912	2713	0·0549	2517	1·66	1·8	5·6
	0·0624	2714	0·0394	2511	1·59	1·4	3·4
	0·0446	2738	0·0293	2503	1·52	1·0	2·5
	0·0390	2720	0·0258	2512	1·51	1·4	3·2
	0·0188	2697	0·0132	2486	1·43	1·6	4·1
	0·0794	2720	0·0563	2541	1·41	1·7	3·4
	0·0696	2713	0·0498	2527	1·40	0·9	3·3
	0·0435	2719	0·0320	2536	1·35	1·1	3·5
	0·0690	2714	0·0520	2524	1·33	1·3	2·6
	0·0748	2713	0·0601	2535	1·23	1·1	3·3
	0·0667	2711	0·0555	2578	1·20	2·1	5·0
IV	0·0993	2706	0·0832	2543	1·19	1·2	3·2
	0·0566	2717	0·0480	2585	1·18	1·0	2·8
	0·0494	2706	0·0416	2607	1·18	0·8	1·7
	0·0801	2715	0·0685	2614	1·16	1·0	2·8
	0·0711	2709	0·0630	2564	1·13	1·4	3·1

By a technique which allows one to increase the spectrophotometric absorption ratio (i.e., the ratio of the absorption intensities at the maximum and the minimum) without greatly reducing the absorption intensity at the maximum at 2710 Å it has been possible to obtain highly stable medicinal liquid paraffin, as was proved by exposure tests of materials after such treatment. This suggests that the Group B compounds are responsible for odour production and for colour development in liquid paraffin, and this view is supported by experiments in which additions were made deliberately of Group A compounds in one series and of Group B compounds in another series to one very pure

liquid paraffin (so as to raise the $E^{1\ per\ cent.}_{1\ cm.}$ – value at 2710Å to a figure of about 0·01). The Group A compounds produced no odour after exposure of the sample to daylight for 5 months, whereas the sample adulterated with Group B compounds acquired an odour after 4 weeks and this unpleasant odour became very distinct after 12 weeks' storage.

It is clear from the spectrophotometric classification that the B.P. acid

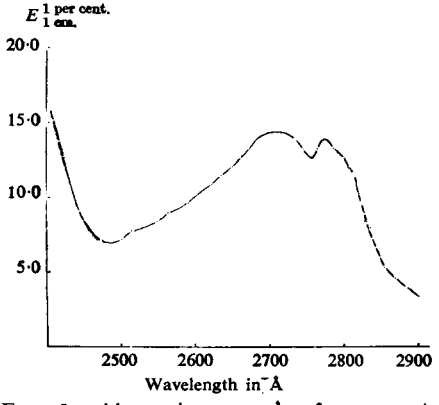

FIG. 3.—Absorption curve of group A compounds isolated from liquid paraffin.

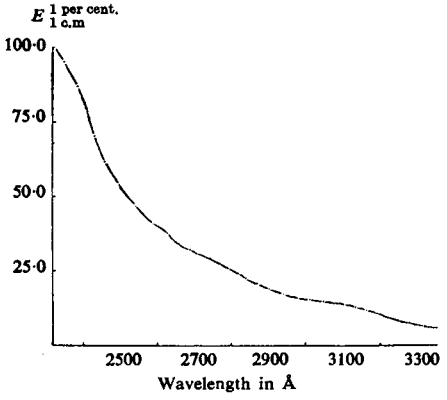

FIG. 4.—Absorption curve of group B compounds isolated from liquid paraffin.

test does not afford a criterion of the quality of medicinal liquid paraffin. Schou and Nielsen[2] in their early examination of 11 samples of medicinal liquid paraffin had arrived at the conclusion that the absorption intensity at about 2730 Å was "in good accordance with the sulphuric acid test for organic impurities," but in the light of the fuller evidence now obtained this view is not borne out. Schou and Nielsen appreciated the advantage of the absorption spectrophotometric examination over the sulphuric acid test of allowing "to express the degree of purity numerically," but they did not proceed to develop a quality and stability criterion, since the aim of their investigation had been to see whether the absorption spectrum could be used to elucidate the origin of the crude oil from which the liquid paraffin had been manufactured.

REFERENCES

1. Martin, *The Physical Meaning of the B.P. Acid Test,* M.Sc. Thesis, London University, 1951.
2. Schou and Nielsen, *Dansk. Tidsskr. Farm.,* 1930, **4,** 1.