

## ANALYTICAL NOTES

TABLE I

Mode of storage	Initial	4 weeks	8 weeks	12 weeks	12 months
(a)	pH 8.18	pH 7.02	pH 6.83	pH 6.69	pH —
(b)	8.17	6.78	6.68	6.56	—
(c)	8.04	8.03	8.01	8.02	7.98

of solution. Table I gives the  $pH$  of the stored solutions after different periods. The solution with added phenol had retained its original  $pH$  and colour whereas the unstabilised solutions became more acidic and reddish in colour; traces of sediment were observed in all 3 solutions. For some years a more sensitive litmus solution has been prepared in these laboratories from the official solution by diluting, and subsequently adjusting the  $pH$ . Litmus solution is prepared as directed in the British Pharmacopœia and 100 ml. of this solution then diluted with 150 ml. of water, just sufficient dilute acetic acid being added to give a very slight red colour. The solution is boiled for a few seconds then cooled and any slight acidity removed by adding dilute solution of ammonia until a purple colour is obtained, followed by boiling. The solution may then be stabilised by the addition of 0.5 g. of phenol per 100 ml. This procedure normally results in a solution having a  $pH$  of 7 to 7.5 but a more accurate adjustment may be made if the  $pH$  be determined during adjustment. Two drops of this stabilised solution in 10 ml. of distilled water gave a reddish-purple colour, changing on the addition of 0.03 ml. of either 0.01N acid or 0.01N alkali. A litmus solution prepared and stabilised as above (initial  $pH$  7.29) was found to be stable during 3 months general laboratory use (final  $pH$  7.26).

## REFERENCE

1. Prideaux, *The Theory and Use of Indicators*, Constable, London, 1917, 354-5.

## (V) THE DETERMINATION OF THE ACID VALUE OF BENZOIN

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IN the official method, a hot ethanolic extract of the material is titrated with ethanolic potassium hydroxide solution, using phenolphthalein as internal indicator. Owing to the dark colouration produced during the titration the end-point is very indistinct and probably appreciably over-run. At the request of the British Pharmacopœia Commission the use of other internal and of external indicators was therefore investigated.

*Internal Indicators.* Using the official method, determinations by several operators on a sample of benzoïn used throughout the work gave results from 117 to 131 (mean 124); no improvement resulted when two similar ethanolic extracts, one only of which contained phenolphthalein, were titrated side by side and compared at equal titres throughout the titration. The experiment was repeated using a photo-electric colorimeter to measure the colours, but in the region of the

expected equivalence-point a slight *decrease* in optical density was noted.  $\alpha$ -Naphtholphthalein, suggested by King,<sup>1</sup> was found to be more suitable than phenolphthalein but the detection of the colour change required considerable practice. The results were somewhat lower than those obtained using the official method.

*External Indicators.* Phenolphthalein papers showed only a transitory pink colour at the end-point, whilst the use of phenolphthalein solution on a "spotting tile" was unsatisfactory since a brown precipitate formed which tended to mask the faint pink end-point colour. However, the addition of the hot extract to about 3 ml. of an aqueous phenolphthalein dilution resulted in a white suspension which aided the detection of the end-point and, moreover, this method gave lower results than the official method. To check accuracy the potentiometric method of Parks and Lykken<sup>2</sup> was applied and the potentiometric end-point was in accordance with that obtained using aqueous phenolphthalein solution as external indicator. Although in a cold *isopropanol*-benzene mixture as used by Parks and Lykken, hydrolysis of balsamic esters was slight, in hot ethanol it was appreciable and since the official method requires the titrated extract to be refluxed for a few minutes to break up any precipitate, it is clearly desirable to prescribe a definite period. Determinations by several operators using the proposed method gave results from 111 to 114 (mean 112.5) as compared with 117 to 131 (mean 124) by the official method.

#### *Proposed Modified Method.*

(a) *Aqueous Phenolphthalein Solution.* Dilute 1 volume of solution of phenolphthalein B.P. with 3 volumes of distilled water.

(b) *Apparatus.* A series of 3 in.  $\times$   $\frac{1}{2}$  in. ignition tubes each containing 3 ml. of aqueous phenolphthalein solution.

(c) *Procedure.* Extract 5 g. of powdered benzoin with 50 ml. of boiling 90 per cent. ethanol by continuous extraction for about 2 hours. Titrate the hot solution with N ethanolic potassium hydroxide until the addition of 0.1 ml. of the solution to the external indicator results, on mixing, in a permanent pink colour. Reheat the solution for a further minute and complete the titration (up to 0.1 ml. of titrant is required).

#### SUMMARY

1. The official method for the determination of the acid value of benzoin has been modified and more precise and accurate results obtained using phenolphthalein as an external indicator.

2. Hydrolysis occurs during the titration and a definite period of reheating after the first end-point is suggested.

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#### REFERENCES

1. King, Private communication to B.P. Commission.
2. Parks and Lykken, *Anal. Chem.*, 1950, **22**, 1444.