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N. N. MURTY and H. K. SEN

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Fluorometric Determination of the Acid & Saponification Values of Lac.

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N. N. Murty and H. K. Sen

(Indian Lac Research Institute, Namkum, Ranchi.)

Introduction.

The determination of the acid and saponification values of lac and its constituents is of great importance in a study of its constitution. In previous publications (1, 3, 5, 6) no fewer than four methods have been described for determining these values, of which the thymol blue method has come into general use. But, in the case of dark coloured lacs (of colour index greater than 20), such as Burma Kusum and saponified solutions of the ether-soluble resin, this indicator fails to give a sharp end point, and in such cases, potentiometric methods have to be employed, despite the long time needed for titration, and the susceptibility of the electrodes to poisoning.

It is well known that the orange yellow colour of an alcoholic solution of lac changes very gradually to pink, starting at a low PH. It is also known (7) that lac exhibits an orange-red fluorescence when exposed to ultra-violet radiation from a mercury arc. During the course of experiment, one of the authors (Murty) found

that when titrated with alkali, this ultra-violet fluorescence of lac changes from orange-red to green, rather sharply near about the end point. The possibility of using this change in the fluorescent colour for fixing the end point of *dark coloured* lac solutions was, therefore, investigated. But it was found that the method works well only with light coloured lac solutions. In the case of dark solutions, however, the addition of β-Naphthol as a fluorescent indicator, while titrating proved very successful.

Experimental.

A description of the changes in colour undergone by an alcoholic solution of lac as titration progresses is given in Table I. It will be seen from this table that within a range of 0.25 c.c. of N/10 alkali, the fluorescence of the lac solution changes to green, brightens up and again becomes slightly darker. With experience, the narrow limits within which the lac solution loses any suggestion of the orange-red fluorescence and assumes a bright parrot-green fluorescence can be detected easily, and an end point in titration with alkali can be fixed. It will be noted, however, that this point is 0.15—0.20 ccs. more towards the acid region than that indicated by thymol blue (as external indicator). After keeping for some time, the green fluorescence becomes somewhat dark and dull.

Table I.

CC. of N/10 alkali for 1 gm. Kusum lac.	Change in Colour.
0.00	Orange-yellow in ordinary light and orange-red in U. V. light.
14.00	Red in ordinary light; no noticeable change in U. V. light.
16.30	Commencement of pink in ordinary light.
17.25	Nearly complete change to pink in ordinary light and commencement of green fluorescence in U. V. light.
17.35	Bright parrot green in U. V. light, with disappearance of any suggestion of orange-red fluorescence. In ordinary light, pink as before which persists).
17.50	Slight darker green fluorescence in U. V. light.
17.55	Change of thymol blue colour from yellow to greenish blue.

SPECTRUM OF THE FLUORESCENT RADIATION

In order to define the fluorescent end point more accurately, the changes in the fluorescent colour were followed with the help of a direct vision spectroscope. In the acid region, the fluorescent radiation from the lac solution consisted of a continuous spectrum of red, yellow and faint green bands. As the titration progressed and the

solution became alkaline, the green band increased in intensity. But contrary to expectation, the red band did not disappear, nor the blue set in. Hence, for finding the end point, reliance has to be placed only on the judgment of the eye and the use of a spectroscope is not of any advantage.

CONSTITUENTS OF LAC WHICH CONTRIBUTE TO FLUORESCENCE.

While the method works well with pale coloured lacs, it was found impossible to detect any sharp change in the fluorescent end point with dark coloured lacs of the type of Burma and Siam lacs. In these lacs, the dye, laccaic acid, which is present in considerably larger proportion than in Indian lacs, may be responsible for masking the end point. A solution of this dye, while exhibiting a brick-red fluorescence in the acid range, shows no fluorescence, and remains dark when rendered alkaline. The resin constituents of lac do not contribute to the fluorescence, as bleached lac does not show any, and carbon-decolourised lac shows but a faint fluorescence. Hence the other colouring matter, namely erythrolaccin, present in lac and not laccaic acid, is responsible for the green fluorescence in the alkaline region. In fact, it is this that serves as a fluorescent indicator during titration in the presence of ultra-violet light.

In order to be able to detect the end point in the case of dark coloured, bleached and carbon-decolourised lacs, a number of fluorescent indicators mentioned by Grant (2) were tried. The indicator quinine, described by Radley (4) as a suitable

fluorescent indicator in acidimetry was found unsuitable, as the change in the fluorescent colour takes place at a very low PH, far removed from the neutral point. Umbelliferone was also found unsuitable, as the change to blue fluorescence is gradual and takes place at a rather low PH. Coumaric acid shows too weak a fluorescence to serve any useful purpose. α-naphthol develops fluorescence at the correct end point ; but the blue fluorescence is not bright enough for use in dark coloured solutions. β-naphthol, on the other hand, suited admirably, as the change to bright violet fluorescence is sharp and takes place at a point between the end points indicated by thymol blue and the bright parrot green fluorescence of lac.

When β-naphthol is added to lac solution, there is a very narrow region (0·05—0·1 c c of N/10 KOH) of dull ash grey fluorescence through which the fluorescent colour of lac changes from bright green to bright violet. That dull ash grey point which is reminiscent of not even the slightest green fluorescence, is taken as the end point of the titration. In the case of very dark coloured lacs, 1 cc. of a one per cent alcoholic solution of β-naphthol will be found to be ample. For light coloured lacs and bleached lacs, a much smaller quantity can be employed. The titration is done in a dark room in a thin walled pyrex or quartz flask, and the reflected fluorescent radiation from the lac solution in flask is viewed at an acute angle to the incident radiation from a mercury arc lamp, filtering through wood's glass. A glass float rendered

fluorescent by filling it with quinine in sulphuric acid is used inside the burette to enable readings being observed as titration proceeds. This obviates the need for having to switch on and off the electric light during the course of the titration. The time occupied in titration under these conditions is no more than in ordinary indicator methods.

This indicator (β-naphthol) has been found useful (table III) in titrating saponified solutions of lac and lac constituents with acids. In tabel II are given the acid values of two varieties of lac obtained by three methods—colorimetric, fluorometric and potentiometric. The electrodes used for the potentiometric method consisted of autimony and quintrydrone electrodes, both dipping into the titration vessel and serving mutually as reference and indicating electrodes. The necessity for establishing liquid junction was thus eliminated. The inflection potentials obtained with this arrangement are of the same order as that obtained with antimony electrode (3), as will be seen from the accompanying curve. From the figures given for acid values in the table, it will be seen that the values obtained with β-naphthol are slightly lower than those obtained with thymol blue, but they correspond more nearly to the values obtained by the potentiometric method. In table IV are given the acid values for some typical lacs and resins which show the general applicability of the fluorescence method.

Table II.

Method.	Acid value.	
	Kusum Shellac.	Palas Shellac.
Sb-quin electrode	71.65	69.51
Thmol blue	71.74	69.95
β-naphthol	71.54	69.18

Table III.

Saponification value.

Sample	S.V. β-naphthol	S.V. Quinhydrone Electrode
Kusum shellac	223.5	224.9
Khair shellac (desiccated)	241.3	241.4
Ether soluble resin (wax-free)	239.5	...
„	216.8	220.6
„	217.7	220.0

Table IV.

Acid value.

Sample No.	Description of sample	Colour index	A.V. β-naphthol.	A.V. quinhydrone.
L227	I. T. N. shellac	23.4	72.52	72.52
*L216	Garnet shellac	41.0	79.40	76.91
*L226	T.N.,(12% rosin)	24.4	85.46	82.57
L224	U. S. S. A. T. N. (0.5% orpiment)	23.0	68.55	67.33
...	Khair shellac	...	71.59	71.74
...	Bleached lac	...	79.6	79.9
...	Rosin	...	160.3	161.0
...	Sandarac	...	128.4	128.5

* In these samples the green colour of the lac solution was so much masked that the end point could be judged only after the manifestation of distinct fluorescence due to β-naphthol. Hence the results are 2-3 per cent higher than those obtained by the potentiometric method.

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Literature Cited.

(1) Gardner, W. H. and W. F. Whitmore ; Ind. Eng. Chem., Anal. Ed., **1**, 205 (1929).

(2) Grant, J. ; Chem. Age ; **34**, 91 (1936).

(3) Murty, N. N. and H. Weinberger ; Ind. Lac. Research Inst. ; Bulletin No. 25, (1936).

(4) Radley, J. A. ; Chem. Age ; **34**, 152 (1936).

(5) Weinberger, H. and W. H. Gardner ; Ind. Eng. Chem., Anal. Ed. **5**, 267 (1933).

(6) Whitmore, W. F. and H. Weinberger with W. H. Gardner ; Ind. Eng. Chem. ; Anal. Ed. **4**, 48 (1932).

(7) Wolff, H. ; "Die Naturlich Harze".