

Note

Separation and identification of impurities in the dye intermediate 8-amino-1-naphthol-3,6-disulphonic acid (H-acid) by high-performance liquid chromatography

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H-acid is the aminonaphthol derivative of naphthalenedisulphonic acid derived from the sulphonation of naphthalene under drastic conditions¹. It is currently used particularly in the manufacture of other important dyes and dye intermediates, principally azo dyes, textile auxiliaries, food dyes, hair dyes and polymer coatings.

The determination of H-acid as obtained from the industrial process was effected in the past by paper² or thin-layer chromatography³, which are time consuming with poor accuracy and precision. A spectrophotometric titration procedure which required derivatization was developed by Kuznetsov *et al.*⁴. High-performance liquid chromatography (HPLC) for the separation of different naphthalenesulphonic acids and their derivatives using sodium sulphate as the mobile phase additive was introduced by Jandera and co-workers^{5–8}. A number of other HPLC methods for the separation of these compounds using efficient anion-exchange methods^{9–13} and tetraalkylammonium salts as ion-pairing agents^{14–23} have been developed. The application of sodium sulphate-containing mobile phases for the quality control of H-acid has been reported²⁴.

The present method involves reversed-phase HPLC using sodium sulphate as the mobile phase with UV detection. Its advantage is the separation of impurities without extraction or derivatization. The method is suitable for monitoring H-acid quality in routine production and allows the determination of purity levels of H-acid without interferences from other dye intermediates.

EXPERIMENTAL

Apparatus

The equipment consisted of a ConstaMetric III dual-piston reciprocating pump (LDC/Milton Roy, Riviera Beach, FL, U.S.A.) and a SpectroMonitor III Model 1204D UV-visible detector (LDC/Milton Roy) with a Rheodyne Model 7125 injector with a 20- μ l fixed loop. The column (250 mm \times 4.6 mm I.D.) contained Spherisorb S5

ODS (5 μm) (LDC/Milton Roy). All chromatograms were recorded on an LDC/Milton Roy Model CI-10 computing integrator with a Sekonics (Tokyo, Japan) printer-plotter.

Reagents and chemicals

Dry, purified sodium sulphate (analytical-reagent grade) was obtained from E. Merck (Darmstadt, F.R.G.). Standards of H-acid, chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulphonic acid), Koch acid (8-aminonaphthalene-1,3,6-trisulphonic acid) and omega acid (8-amino-3-naphthol-1,6-disulphonic acid) from Zenith Chemicals (Boisar, Tarapur, India) and G-salt (2-naphthol-6,8-disulphonic acid) and Nevile-Winther acid (1-naphthol-4-sulphonic acid) from Sahyadri Dyestuff (Pune, India). Doubly distilled, deionized water was used for preparing mobile phase, standard and sample solutions (500 $\mu\text{g}/\text{ml}$ each). The samples of H-acid were supplied by Zenith Chemicals.

The mobile phase was 0.30 *M* sodium sulphate at a flow-rate of 1.0 ml/min. The UV-visible detector was set at 235 nm with a sensitivity of 0.05 a.u.f.s.

RESULTS AND DISCUSSION

In the manufacture of H-acid, isomers of disulphonic acids, namely chromotropic acid and omega acid, and Koch acid, a trisulphonic acid, are also formed in appreciable amounts. Their structures are shown in Fig. 1. Fig. 2 shows a typical chromatogram obtained from a sample of H-acid. Reference standards of Koch acid, omega acid and chromotropic acid were injected separately in order to confirm the identities of the components in the sample of H-acid. Unknown concentrations in the H-acid sample were obtained by using the equation:

$$\text{Unknown concentration } (X_i) = \text{response factor } (\text{RF})_{(X_i)} \times \text{area } (X_i)$$

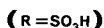
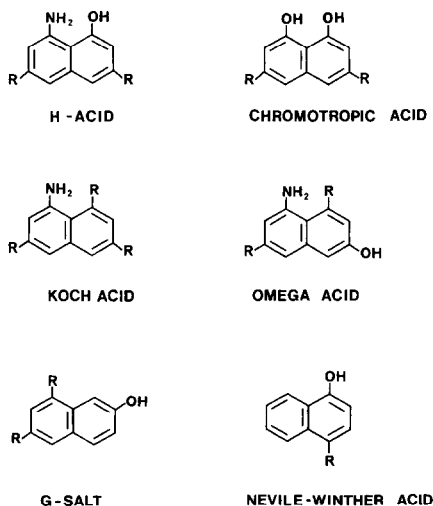


Fig. 1. Structures of dye intermediates.

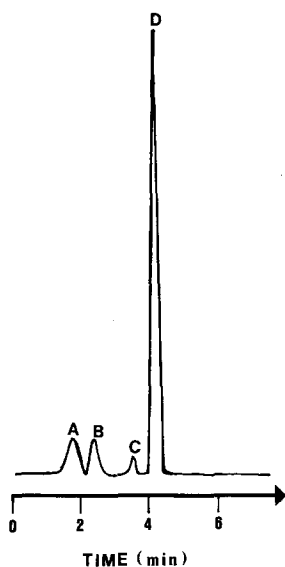


Fig. 2. Chromatogram of H-acid sample (500 $\mu\text{g/ml}$). Peaks: A = Koch acid; B = omega acid; C = chromotropic acid; D = H-acid.

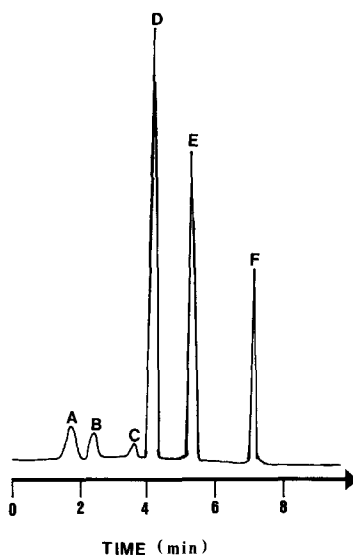


Fig. 3. Chromatogram of a mixture containing 500 $\mu\text{g/ml}$ each of G-salt, Nevile-Winther acid and H-acid. Peaks: A = Koch acid; B = omega acid; C = chromotropic acid; D = H-acid; E = G-salt; F = Nevile-Winther acid.

where X_i is either H-acid or impurities present in H-acid, and $(\text{RF})_{(X_i)}$ the response factor of H-acid or impurities.

TABLE I

SUMMARY OF METHOD VALIDATION DATA FOR THE DETERMINATION OF H-ACID OBTAINED FROM INDUSTRIAL SULPHONATION

Concentration added ($\mu\text{g/ml}$)	Concentration found ($\mu\text{g/ml}$) (mean \pm standard deviation, $n = 15$)	Relative standard deviation (%)
<i>Within-day variation:</i>		
100	99.5 \pm 0.11	0.11
150	148.8 \pm 0.12	0.08
250	249.9 \pm 0.14	0.05
350	350.0 \pm 0.16	0.04
400	398.5 \pm 0.19	0.04
<i>Day-to-day variation:</i>		
100	98.5 \pm 0.10	0.10
150	149.5 \pm 0.11	0.07
250	250.0 \pm 0.13	0.05
350	348.9 \pm 0.16	0.04
400	399.9 \pm 0.20	0.05

The method was applied to the separation of other commonly used dye intermediates, G-salt and Neville–Winther acid, the structures of which are shown in Fig. 1. A chromatogram resulting from a mixture of H-acid, G-salt (peak E) and Neville–Winther acid (peak F) is shown in Fig. 3. Both the components added were well separated and do not interfere with H-acid or its impurities.

A calibration graph was prepared for H-acid and for impurities such as omega acid, chromotropic acid and Koch acid in the concentration range 100–500 $\mu\text{g/ml}$. The regression equations (with x = concentration of the component and y = peak area of the component) were $y = 0.0165x + 1.0485$, $y = 0.0819x + 0.8564$, $y = 0.0183x + 2.1325$ and $y = 0.0523x + 0.5529$ for H-acid, omega acid, chromotropic acid and Koch acid, respectively. Each point on the calibration graph was measured at least ten times. The detection limits were found to be 105 $\mu\text{g/ml}$ for H-acid, 120 $\mu\text{g/ml}$ for omega acid, 140 $\mu\text{g/ml}$ for chromotropic acid and 110 $\mu\text{g/ml}$ for Koch acid at 235 nm, 0.05 a.u.f.s.

Results of the method validation study for H-acid samples are shown in Table I. The reproducibility of the analytical procedure was obtained by determining the within-day and day-to-day variations. The relative standard deviations for five different concentrations in both instances varied between 0.04 and 0.11%, demonstrating excellent precision.

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