A simple HPLC method for determination of 2-diazonaphthoquinone-5-sulphonic acid phenyl ester used in positive photoresists

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A simple high performance liquid chromatographic (HPLC) method for the determination of 2-diazonaphthoquinone-5-sulphonic acid phenyl ester (DNQ) is developed. 5-Amino naphthalene-1-sulphonic acid sodium salt is used as internal standard. A Polaris C18-5 μ silica column (250×4.6 mm), 5 μ particle size, was equilibrated with a mobile phase composed of methanol and water (80:20, v/v). Flow rate was 1.0 mL/min. The elution time for 5-amino naphthalene-1-sulphonic acid sodium salt and DNQ was approximately 2 and 4 min, respectively. Calibration curve of DNQ was linear in the concentration range of 10-50 μg/mL. Limit of detection and quantification were measured in the lowest concentrations of the replicates. Recovery is about 96%.

Keywords: 2-Diazonaphthoquinone-5-sulphonic acid phenyl ester, 5-Amino naphthalene-1-sulphonic acid sodium salt, Reverse phase HPLC, Quantification, HPLC method validation

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Diazonaphthoquinone derivatives are very important materials in photoresists. These photoresists have applications in photolithography, photo fabrication process and electronic industry. 2-Diazonaphthoquinone-5-sulphonic acid phenyl ester (DNQ) is used as a photoactivating compound in positive photoresists. Photoactivating compound present in the positive photoresists undergoes chemical change upon exposure to light of proper wavelength, which renders the polymer soluble in an alkaline developer. The mechanism involved in this process is the photoactivating compound upon exposure to UV radiation generates a highly reactive intermediate, ketene. This intermediate reacts with additive material (H2O) leading to indene carboxylic acid derivative, which is soluble in alkaline developer solvent. The differential solubility rate between exposed and unexposed areas allows the transfer of the images of circuit elements from a patterned photo mask into developed resist images with tight control of their physical dimensions. Although there are methods for making DNQ, but there is no HPLC quantification method reported in the literature and this has prompted us to develop an HPLC validation method.

Experimental Procedure

2-Diazonaphthoquinone-5-sulphonic acid phenyl ester (1) was prepared under modified conditions of earlier reported methods and analyzed by HPLC method.

Instrumentation

A Shimadzu (Kyoto, Japan) LC-10AT pump was used to deliver the mobile phase to the analytical column, Polaris C18-5 μ silica column with 250×4.6 mm diameter purchased from Supelco (USA). Sample injection was performed via Rheodyne 7125 injection valve (Rheodyne, USA) with a 20 μL loop. Detection was achieved by an SPD-10VP UV detector (Shimadzu, Japan). C-R8A integrator (Shimadzu, Japan) was used for quantitative determination of eluted peaks. Degassing of solvents was achieved by helium purging before use. Dissolution of compound was enhanced by sonication on Bandelin sonerex (Bandelin, Berlin). Perkin-Elmer UV-Visible spectrophotometer was used to generate UV-Visible absorption spectra to select working wavelength of detection.

Standards and Chemicals

All chemicals were of analytical purity grade. 5-Amino-1-naphthalene sulphonic acid sodium salt (2) was purchased from Fluka Chemicals. HPLC grade methanol solvent was purchased from S.D. Fine Chem. Ltd, Mumbai, India. Purified water was prepared using a Millipore Milli-Q (Bedford, M.A., USA) water purification system.
Chromatographic conditions

The mobile phase used in this study was methanol and water (80:20, v/v) with a flow rate of 1 mL per min. The mobile phase was filtered using 0.4 μm membrane filters and degassed before use. All the experiments were carried out at ambient temperature. The detection was carried out at 335 nm. The identification of 2-diazo-1-naphthoquinone-5-sulphonyl phenyl ester and 5-amino naphthalene-1-sulphonic acid sodium salt was confirmed by running the chromatograms of the individual compounds under identical chromatographic conditions. The elution time of 5-amino naphthalene-1-sulphonic acid sodium salt and DNQ was approximately 2 and 4 min, respectively. Since DNQ is light sensitive, hence the operations were carried out in yellow/dark room conditions.

Preparation of standards

Stock solutions of DNQ and 5-amino naphthalene-1-sulphonic acid sodium salt were prepared by dissolving 100 mg of DNQ and 100 mg of 5-amino naphthalene-1-sulphonic acid sodium salt separately in 100 mL standard volumetric flasks containing 70 mL of methanol, sonicated for about 20 min and then made up to the volume with methanol. Daily working standard solutions of DNQ and 5-amino naphthalene-1-sulphonic acid sodium salt were prepared by suitable dilution of the stock solution with mobile phase. These stock solutions can be stored in a dark room for about a week.

Results and Discussion

Linearity

To establish the range of linearity between compound concentration and detector response, five separate series of solutions of the compound 10-50 μg/mL were prepared from the stock solution and analyzed. Five replicates of analyte were measured. Regression analysis was performed for the ratios of peak areas of DNQ to that of 5-amino naphthalene-1-sulphonic acid sodium salt.

Figure 1 illustrates HPLC chromatograms of blank spiked with 100 μg/mL of 5-amino naphthalene-1-sulphonic acid sodium salt and blank spiked with 100 μg/mL of DNQ. The total eluting time was less than 10 min. The regression lines related to standard concentrations of DNQ and 5-amino naphthalene-1-sulphonic acid sodium salt peak ratios were calculated using weighed regression analysis [(weight + 1/(concentration))^2], the calibration curves were linear under the limited concentration range of DNQ (Fig. 2).

The mean standard deviation (SD) for the slope, intercept and correlation coefficient of standard curves (n = 5) were calculated. The representative data is included in Table 1.

Limit of detection (LOD)

The limit of detection can be defined as the smallest level of analyte that gives a measurable response. The LOD is based on signal-to-noise (S/N) ratio typically 3.0 for HPLC methods. Five replicates of analyte were measured.
Table 1—Recovery studies of 2-diazo-1-naphthoquinone-5-sulphonyl phenyl ester

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Nominal concentration (μg/mL)</th>
<th>Measured concentration (μg/mL) ± SD</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>19.20 ± 1.0</td>
<td>96.0</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>29.02 ± 0.7</td>
<td>96.7</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>38.60 ± 0.5</td>
<td>96.5</td>
</tr>
</tbody>
</table>

\* SD is the standard deviation of the mean %recovery; standard solutions were prepared and measured in triplicate.

Limit of quantification (LOQ)

Limit of quantification—the lowest concentration at which the precision was expressed by relative standard deviation (RSD), is less than 20%, and accuracy expressed by relative difference in the measured and true value was also less than 20%. In other words, the analyte response is 10 times greater than the noise response. Five replicates of analyte were measured and quantified.

Recovery

Percentage elution of compound from spiked blank were determined and represented as mean ± standard deviation by injecting quality control samples of five replicates. The recovery data of DNQ is given in Table 1.

Accuracy

Accuracy was evaluated by assaying quality control with different concentrations of compound. From recovery studies, accuracy was assessed by analyzing four quality control samples at each concentration. Accuracy was presented as percent error (relative error), \([(\text{measured concentration-added concentration})/\text{added concentration}] \times 100\%\).

Conclusion

A simple, fast and reliable reversed phase HPLC method with UV-Visible spectrometric detection for the determination of 2-diazonaphthoquinone-5-sulphonic acid phenyl ester has been optimized and validated. Better recovery at lower concentrations was achieved successfully.

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