Ultrathin-Layer Chromatography on Nanoengineered Thin Films

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Chevron Media
Blade-Like Media
Overview

- Higher performance with nanostructuring
- Glancing angle deposition (GLAD)
- GLAD ultrathin-layer chromatography (UTLC) microstructures
- Channel features in anisotropic GLAD UTLC media and their effects on elution
- Final thoughts

Diagonal dye separation pattern on an anisotropic ultrathin-layer chromatography plate fabricated using glancing angle deposition

Figure from S.R. Jim et al., Anal. Chem. (2010).
### Higher Performance with Nanostructuring

<table>
<thead>
<tr>
<th>Stationary Phase Layer Properties</th>
<th>TLC $^{1,2}$ (particles, silica gel 60)</th>
<th>HPTLC $^{1,2}$ (particles, silica gel 60)</th>
<th>UTLC $^{1-3}$ (monolithic, silica gel)</th>
<th>GLAD UTLC $^{4-7}$ (columnar SiO$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical Thickness ($\mu$m)</td>
<td>100 – 250</td>
<td>100 – 200</td>
<td>10</td>
<td>4.5 – 5</td>
</tr>
<tr>
<td>“Characteristic” Size ($\mu$m)</td>
<td>10 – 12 (mean particle size)</td>
<td>4 – 6 (mean particle size)</td>
<td>1 – 2 (macropore size)</td>
<td>0.1 – 0.8 (intercolumn void)</td>
</tr>
<tr>
<td>Pore Size (Å)</td>
<td>60</td>
<td>60</td>
<td>30 – 40</td>
<td>20 – 40</td>
</tr>
<tr>
<td>Specific Surface Area (m$^2$ g$^{-1}$)</td>
<td>520</td>
<td>480 – 540</td>
<td>~ 350</td>
<td>~ 450</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Representative Elutions</th>
<th>TLC $^{1-3}$</th>
<th>HTLC $^{1,2}$</th>
<th>UTLC $^{1-3}$</th>
<th>GLAD UTLC $^{4,5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Development Time (s)</td>
<td>&gt; 900</td>
<td>&gt; 180</td>
<td>60 – 360</td>
<td>&lt; 90</td>
</tr>
<tr>
<td>Development Distance (mm)</td>
<td>70 – 150</td>
<td>30 – 70</td>
<td>10 – 30</td>
<td>10 – 14</td>
</tr>
<tr>
<td>Limit of Detection (ng, absorption)</td>
<td>1 – 5</td>
<td>0.1 – 0.5</td>
<td>0.5</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>Theoretical Plate Height ($\mu$m)</td>
<td>30 – 75</td>
<td>12 – 25</td>
<td>80 $^3$</td>
<td>12 – 30</td>
</tr>
</tbody>
</table>

Glancing Angle Deposition (GLAD) and UTLC Microstructures

Shadowing and Sculpting Architectures, Advantages, and Applications
GLAD Microstructures and Elution Channel Features in Anisotropic Media Migration in Anisotropic Microstructures
Shadowing and Sculpting

Glancing angle deposition couples self-shadowing with substrate motion control to sculpt columnar thin films of useful morphologies.

Figure from S.R. Jim et al., Anal. Chem. (2010).
Architectures, Advantages, and Applications

Representative scanning electron micrographs of GLAD morphologies

- **Key Capabilities**
  - Excellent control over porosity and architecture
  - Variety of materials
  - Patented single-step technology compatible with microfabrication

- **Applications**
  - Rapid relative humidity sensors
  - Optical and photovoltaic devices
  - Planar chromatography

(a) Vertical post, (b) chevron, (c) blade-like, (d) helical, (e) nanoribbon, and (f) hybrid structures.

GLAD Microstructures and Elution

Micrographs of macroporous GLAD thin film separation media

Vertical Post (Isotropic)  Chevron (Anisotropic)  Blade-Like (Anisotropic)

Scanned images of developed GLAD UTLC plates

Vertical Post (Isotropic)  Chevron (Anisotropic)  Blade-Like (Anisotropic)

Channel Features in Anisotropic Media

- Development track deviation angle ($\Delta \theta$) as a measure of the “extent of anisotropy”:

\[ \Delta \theta = \theta_C - \theta_T \] 

(1)

Figure modified from S.R. Jim et al., Anal. Chem. (2010).
Migration in Anisotropic Microstructures

\[ \alpha = 82.5^\circ \] \hspace{1cm} \[ \alpha = 84^\circ \] \hspace{1cm} \[ \alpha = 85.5^\circ \] \hspace{1cm} \[ \alpha = 87^\circ \]

Low and high magnification top view SEM micrographs of \( \sim 5 \mu m \) thick SiO\(_2\) blade-like films fabricated with varied deposition angle (\( \alpha \))

Figure modified from A.J. Oko \textit{et al.}, \textit{Anal. Chem.} (2011).
Migration in Anisotropic Microstructures

Along-channel ($\theta_C = 0^\circ$) chromatograms for GLAD UTLC plates of varied porosity (varied deposition angle, $\alpha$)

Chromatograms for $\alpha = 87^\circ$ blade-like plate with channels oriented at varied angles ($\theta_C$)

Final Thoughts

Conclusions
Acknowledgements
Further readings on the GLAD technique and on GLAD UTLC
Conclusions

• Planar chromatography performance improves with stationary phase microstructure engineering.

• GLAD provides excellent control over the porosity and architecture of columnar UTLC microstructures.

• Anisotropic GLAD UTLC media exhibit channel features that strongly influence analyte migration velocities, separation track orientations, and spot broadening.

• Ongoing research aims to combine the benefits of anisotropic media with post-processing and better-suited chromatography instrumentation to produce a high-performance GLAD UTLC system.
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• RIE help from S. Munro (NanoFab)
• Custom apparatus fabrication (U of A ECE Machine Shop)
Further reading on GLAD UTLC


Further reading on the GLAD technique and applications


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