Inkjet application, chromatography and mass spectrometry of sugars on nanostructured thin films

S. Kirchert[1] , Z. Wang[2], M. Taschuk[2], S. Jim[2], M. Brett[2,3], G. Morlock[1]

[1]Justus Liebig University of Giessen, Germany
[2]University of Alberta, Edmonton, Canada
[3]NRC National Institute for Nanotechnology, Edmonton, Alberta, Canada

Introduction

One of the newest technologies for manufacturing miniaturized tailored layers in the field of planar chromatography is glancing angle deposition (GLAD) which started in 2001. Main differences like shorter migration distances, faster development, lower specific surface area (UTLC: 150 - 350 m^2/g, HPTLC: 500 m^2/g), and less solvent and sample use were already discussed in numerous papers [1, 2, 3]. Invention of miniaturized UTLC films led to the novel concept of office chromatography [1, 3]. Office chromatography combines print and media technologies with chromatography and it offers the possibility of a miniaturized one-click planar chromatographic system [3]. The current problem is that no working system is available for UTLC plates. All systems are optimized for HPTLC plates. Nevertheless, first office chromatographic methods were shown for authorized water-soluble dye [4, 5] and sugar separations [6] on GLAD-UTLC films.

Results and discussion

Method development

For the sugar separation on GLAD-UTLC films, the first derivatization on these films was demonstrated. The stationary phase used was a 5 µm silicon dioxide nanostructured thin film that was produced through GLAD. To optimize the stationary phase and the separation the density of the film was reduced. Application of sharp water-soluble sugar bands of 7 - 25 nL volumes was performed with a Canon inkjet printer.

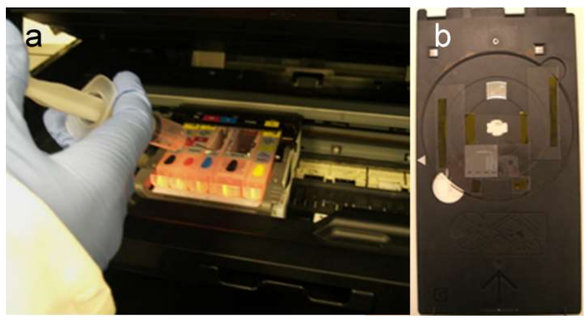

Fig. 1 Printer: Cartridge filling (a) and CD tray with GLAD-UTLC film (b)

The printer cartridges (with cut, open top and removed sponge) were filled with a syringe (Fig. 1). A computer program controlled the printer, which allowed deactivation of four of the five cartridges, the remaining one was used for sample dosage. The GLAD-UTLC film was placed on a prepared CD-tray (Fig. 2).

The plate was aligned with small glass pieces fixed on the CD-tray with double-sided tape. Created by Adobe Illustrator, a pattern with four bands (3 mm x 0.1/0.2/0.3/0.4 mm) was printed. After drying the start zones, chromatography was performed in a special horizontal UTLC chamber [7] with a mixture (2 mL) of ethyl acetate, methanol, formic acid and water 8:2:1:0.5 (v/v/v/v) in 4 min. The reduced specific surface area of the GLAD film required a reduction in mobile phased polarity. Sugars are very polar analytes, so in combination with a too polar mobile phase [7] they were not retarded on the GLAD films. So the mobile phase was adjusted. The GLAD-UTLC films were placed face down on the frit and aligned against a small glass spacer.

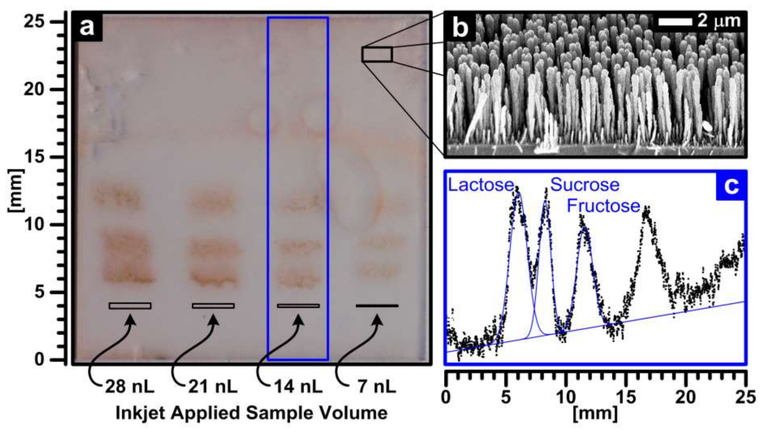

Fig. 2 Sugar samples on miniaturized planar chromatography plates (a) fabricated from nanostructured silica GLAD thin films (b). The separated sugars were derivatized by spraying with the β-naphthol reagent. Exemplarily, a densitogram of a track is shown (c; blue box: 26 mm x 47 mm).

Derivatization followed with β-naphthol reagent (Fig. 2). The films were derivatized by spraying. GLAD-UTLC chromatograms were documented with a camera [6]. For each track, a densitogram was produced showing the good separation of the four sugars.

Fig. 3 Chocolate sample [8]

Milk chocolate analysis

The miniaturized technique was applied to actual food samples such as chocolate (Fig. 3). The dissolved sample solution was diluted to a total sugar concentration of 2.3 % to avoid the risk of nozzle clogging due to the very high sugar concentration. This sample was printed with descending mass loadings (660 to 70 ng/band; Fig. 4, tracks 1 – 6; track 7 below LOD).

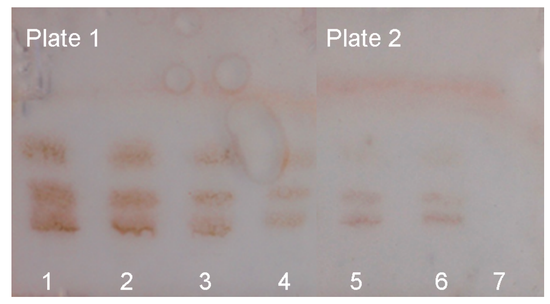

Fig. 4 Chocolate sample separation on two 5 mm VP 86° SiO_2 plates with descending mass loadings.

Hyphenation of GLAD films and ESI-MS

The zone of interest was tightly fixed with the circular cutting edge of the elution head (TLC-MS Interface). A glucose solution was applied on the GLAD-UTLC phase, dried and used for recording of mass spectra without development and derivatization. This measurement provided two hexose signals in both ion modes (Fig. 5).

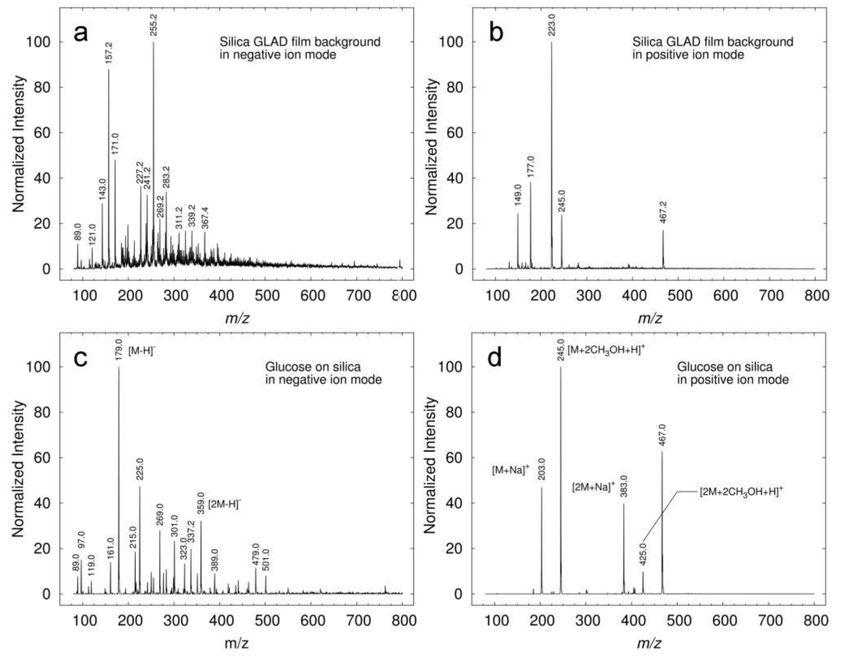

Fig. 5 Mass signals on the GLAD-UTLC 5 µm VP SiO_2 layers: background (a, b) and glucose zone (c, d)

In the negative ion mode, the base peak was the deprotonated hexose molecule at *m/z* 179 $[Glc\text{-}H]^-$, but also its deprotonated dimer was evident at *m/z* 359 $[2Glc\text{-}H]^-$. In the positive ion mode the respective sodium adduct of the hexose molecule at *m/z* 203 $[Glc+Na]^+$ and *m/z* 383 $[2Glc+Na]^+$ were clearly visible. The measured background of the silicon dioxide GLAD-UTLC layers showed background signals, which could repeatedly be found in the spectra in both ionization modes. Further on, the applied glucose solution was derivatized with the 2-naphthol reagent. The reagent background was measured and subtracted from the glucose derivative spectrum. The resulting mass spectrum showed several signals and it was possible to identify glucose in the positive ion mode at *m/z* 181 $[Glc+H]^+$ and *m/z* 361 $[2Glc+H]^+$, however, not the derivatization product.

Conclusions

A first successful separation and derivatization demonstrated the potential of GLAD-UTLC layers in food chemistry and confirms its integration into the office chromatography concept. Underivatized sugars were detected through the use of mass spectrometry, demonstrating the possibility of coupling the advantages of miniaturized GLAD-UTLC layers with MS.

References [1] G. Morlock, Analytik News (2010) 1-5, [2] G. Morlock, C. Oellig, L. W. Bezuidenhout, M. J. Brett, W. Schwack, Anal. Chem. 82 (2010) 2940-2946, [3] A. Matheson, G. Morlock, LCGC Eur. 23 (2010) 1-4, [4] C. Oellig, diploma thesis, University of Hohenheim, [5] J. Wannenmacher, S. R. Jim, M. T. Taschuk, M. J. Brett, G. E. Morlock, J. Chrom. A 1318 (2013) 234-243, [6] S. Kirchert , Z. Wang, M. T. Taschuk, S. R. Jim, M. J. Brett, G. E. Morlock, Anal. Bioanal. Chem. 405 (2013) 7195-7203, [7] G. Morlock, G. Sabir, J. Liq. Chromatogr. Relat. Technol. 34 (2011) 902-919, [8] www.thefloridastandard.com/2013/05/27/cadburys-milk-chocolate.

Thanks to DAAD PPP Canada for funding and Micralyne, the Natural Sciences and Engineering Research Council of Canada and Alberta Innovates for financial support.

IFZ Interdisziplinäres Forschungszentrum Giessen Research Centre for BioSystems, Land Use and Nutrition

Food Science, Justus Liebig University Giessen, Institute of Nutritional Science, Heinrich-Buff-Ring 26-32, 35392 Giessen, Germany