Aalto University
School of Chemical
Technology

Thin layer chromatographic behaviour of dyes during microfluidic transport in functionalised calcium carbonate coatings

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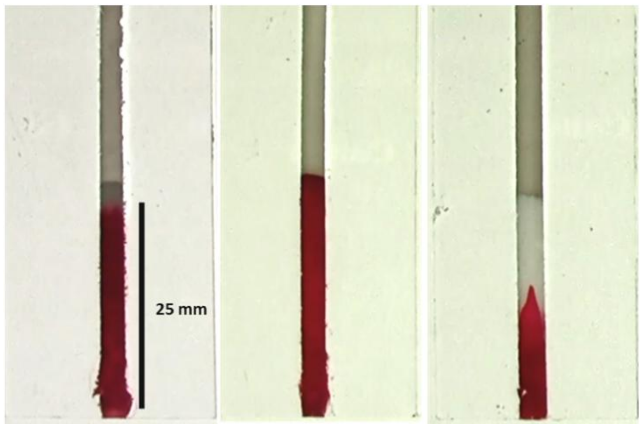
Background

Background 1/4:
Aims of the Research

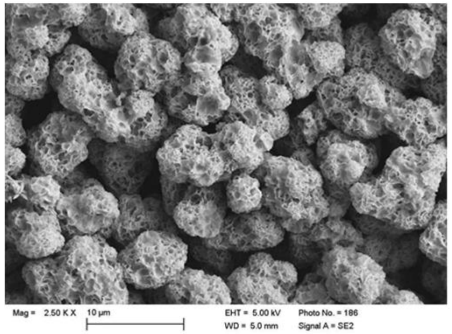
– **New applications for functionalised calcium carbonate (FCC) based coatings, such as**
  - Microfluidic devices
    - *Paper-based reaction arrays*
    - *Paper-based enzymatic assays*
  - **FCC-based TLC plates (today's subject)**

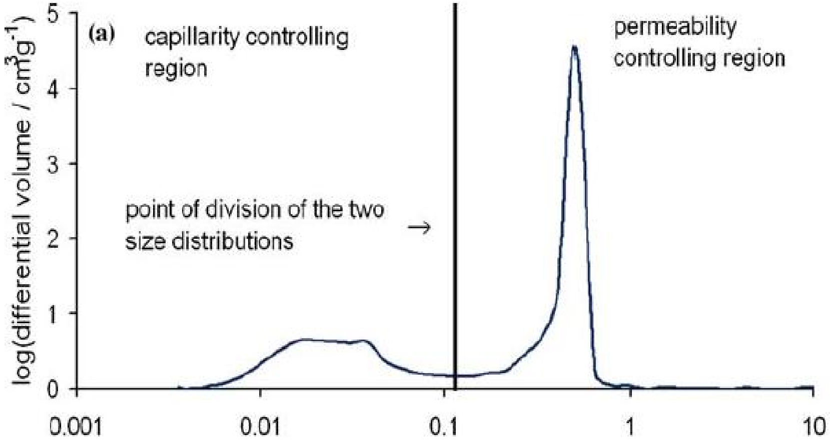
- **Possible applications**
  - Medical diagnosis
  - Environmental monitoring
  - Laboratory research tools
- **Novelty: <u>custom paper coatings</u>**



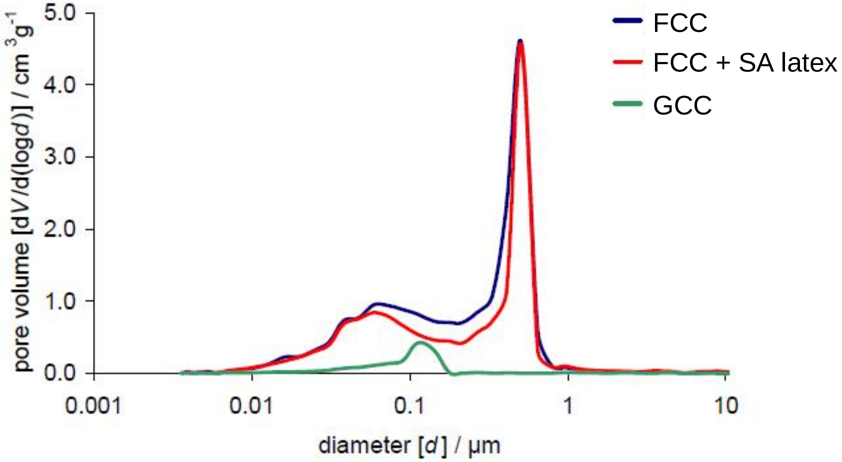
Background 2/4:
Functionilised Calcium Carbonate (FCC)

- based on ground calcium carbonate (GCC) with specific surface and internal structure modifications
- discretely bimodal pore size distribution
    - inter and intraparticle pores
- fast absorption by high capillarity in internal (intraparticle) pores and high permeability through interparticle voids





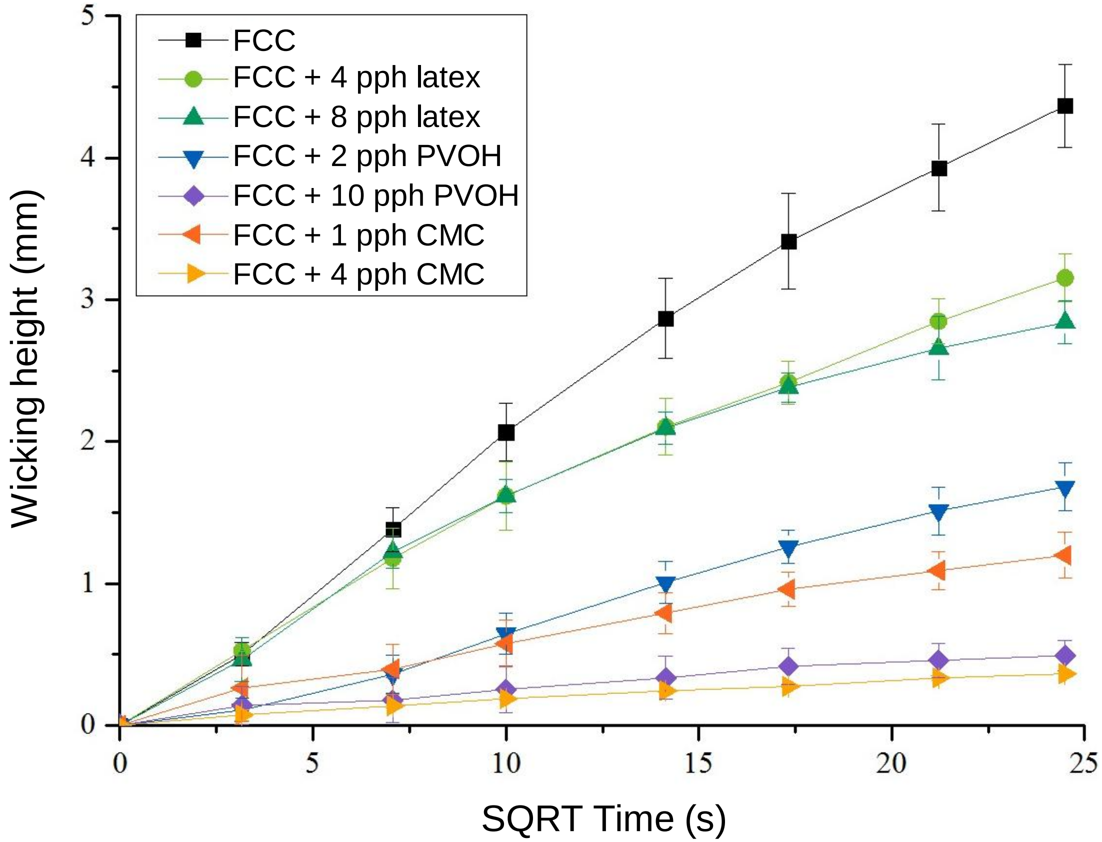
Ridgway *et al*. Trans. Porous. Med., 2006, 63, 239-259.



Ridgway *et al*. Proceedings of PaperCon'11, 2011, 1305-0319.

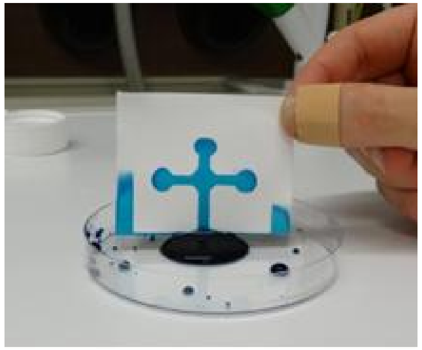
Background 3/4:
FCC as Wicking Medium

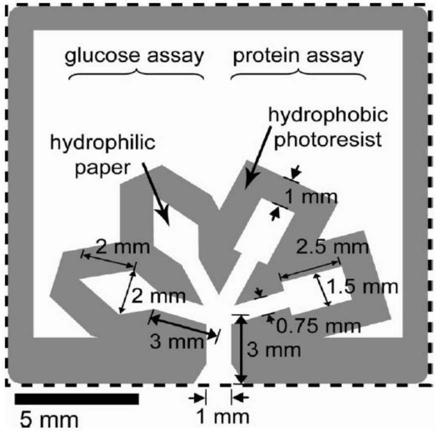
Wicking of liquids in FCC coatings



Jutila, *et al.*, J. Print Media Technol. Res., in the review process.

FCC-based microfluidic test

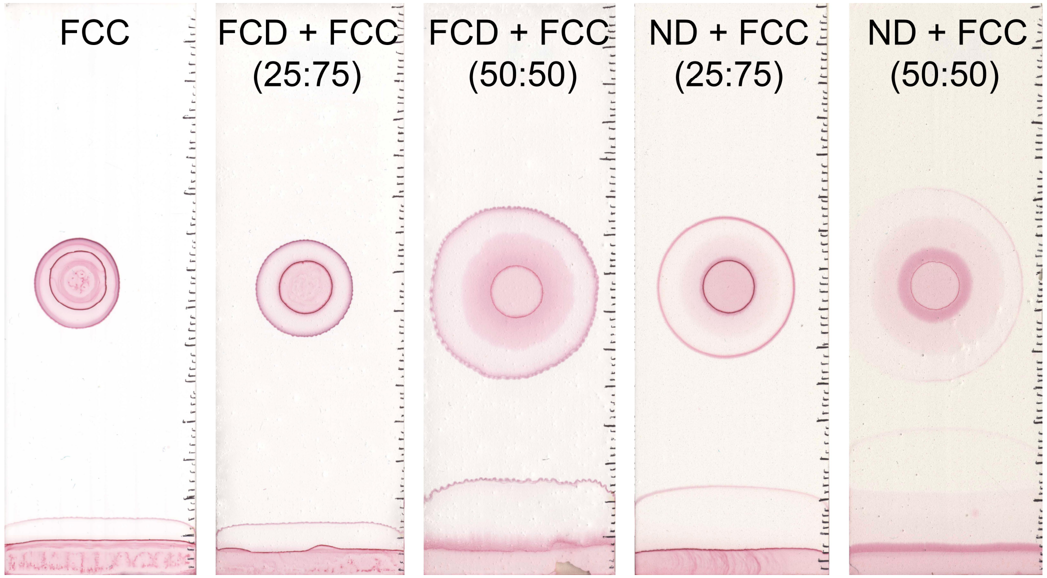




Martinez, *et al*. Anal Chem, 2008, 80(10), pp.3699-3707.

Background 4/4:
FCC as Wicking Medium

Charge separation-induced chromatographic behaviour of dyes during microfluidic transport



FCC = functionalised calcium carbonate
FCD = flux-calcined diatomite
ND = natural diatomite

Jutila, *et al*., J. Print Media Technol. Res., in the review process.

– Could FCC coatings be used as thin layer chromatography (TLC) ab/adsorbent?

– What effect would surface area, porosity and chemical charge of the coating have on the component separation in TLC experiments?

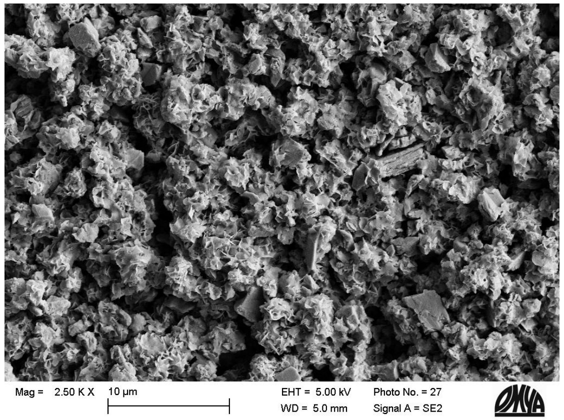
Experimental

Experimental 1/7:

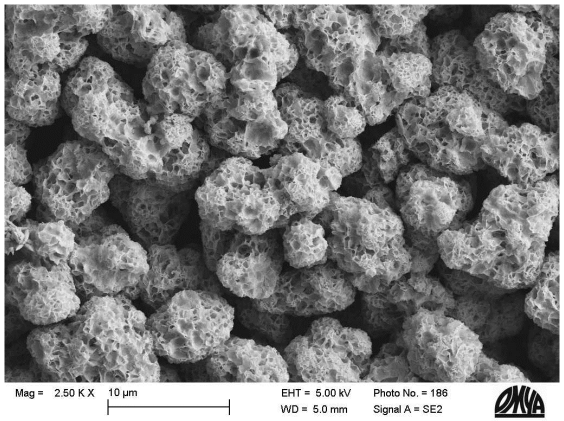
Materials – Pigments and Polymers

- pharmaceutical grade of (FCC)
  - hydrophilic, high absorption capacity
  - three different specific surface areas: 40, 105 and 160 m^2g^{-1}
- charge modifiers:
  - anionic (An) – sodium polyacrylate (Coatex S.A.)
  - cationic (Cat) – polyDADMAC (Sigma-Aldrich)

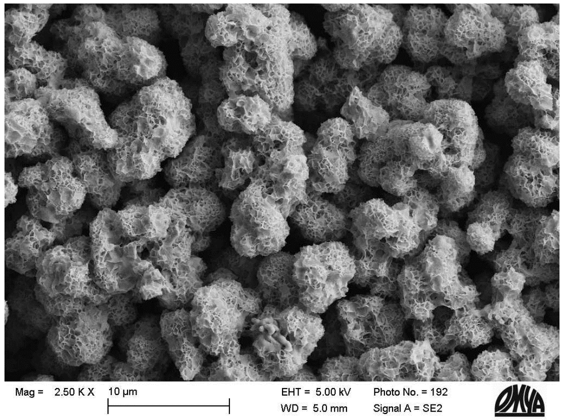
FCC(40)



FCC(105)

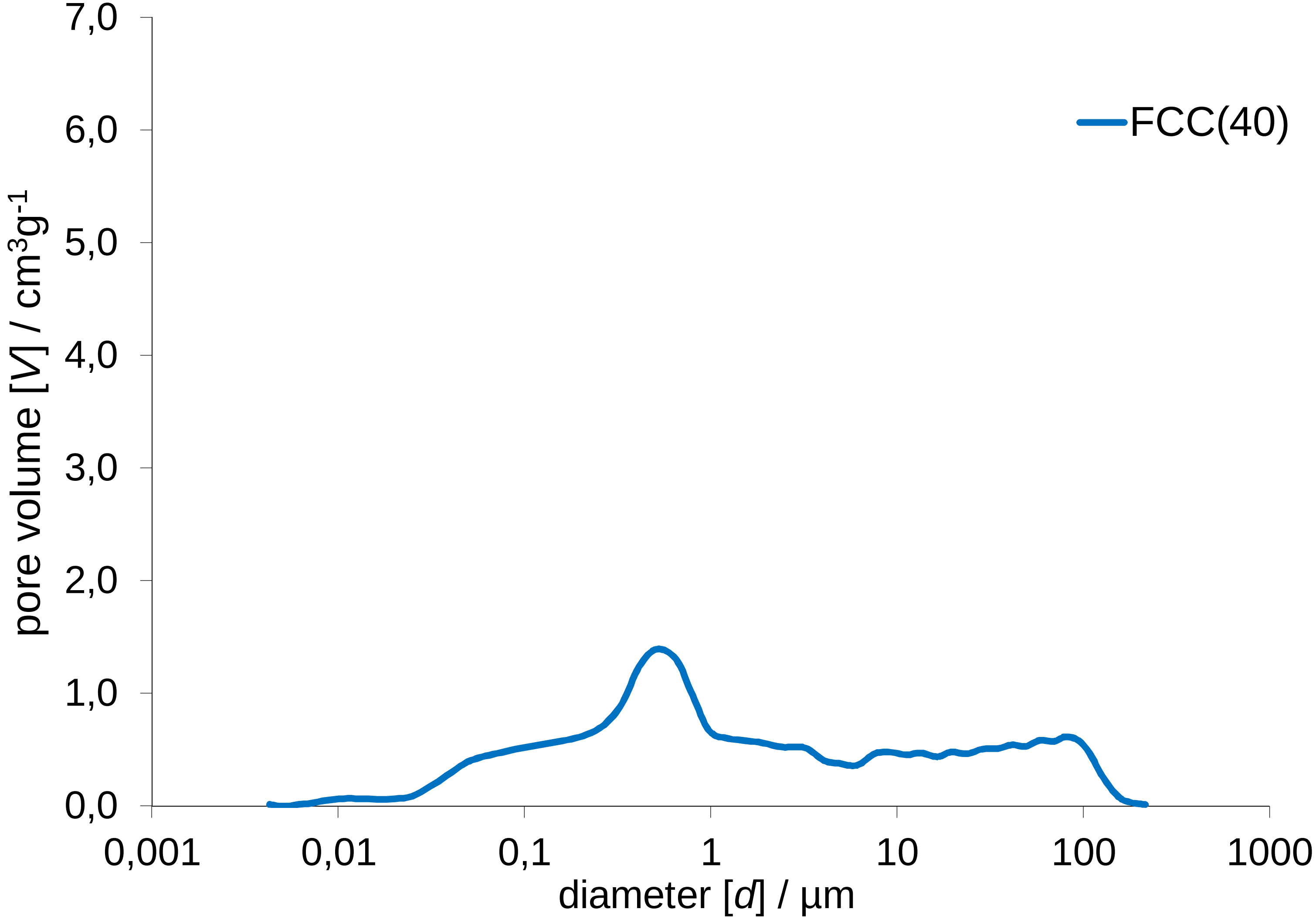


FCC(160)



Experimental 2/7:

Pore Size Distribution of Pigments



Experimental 2/7:

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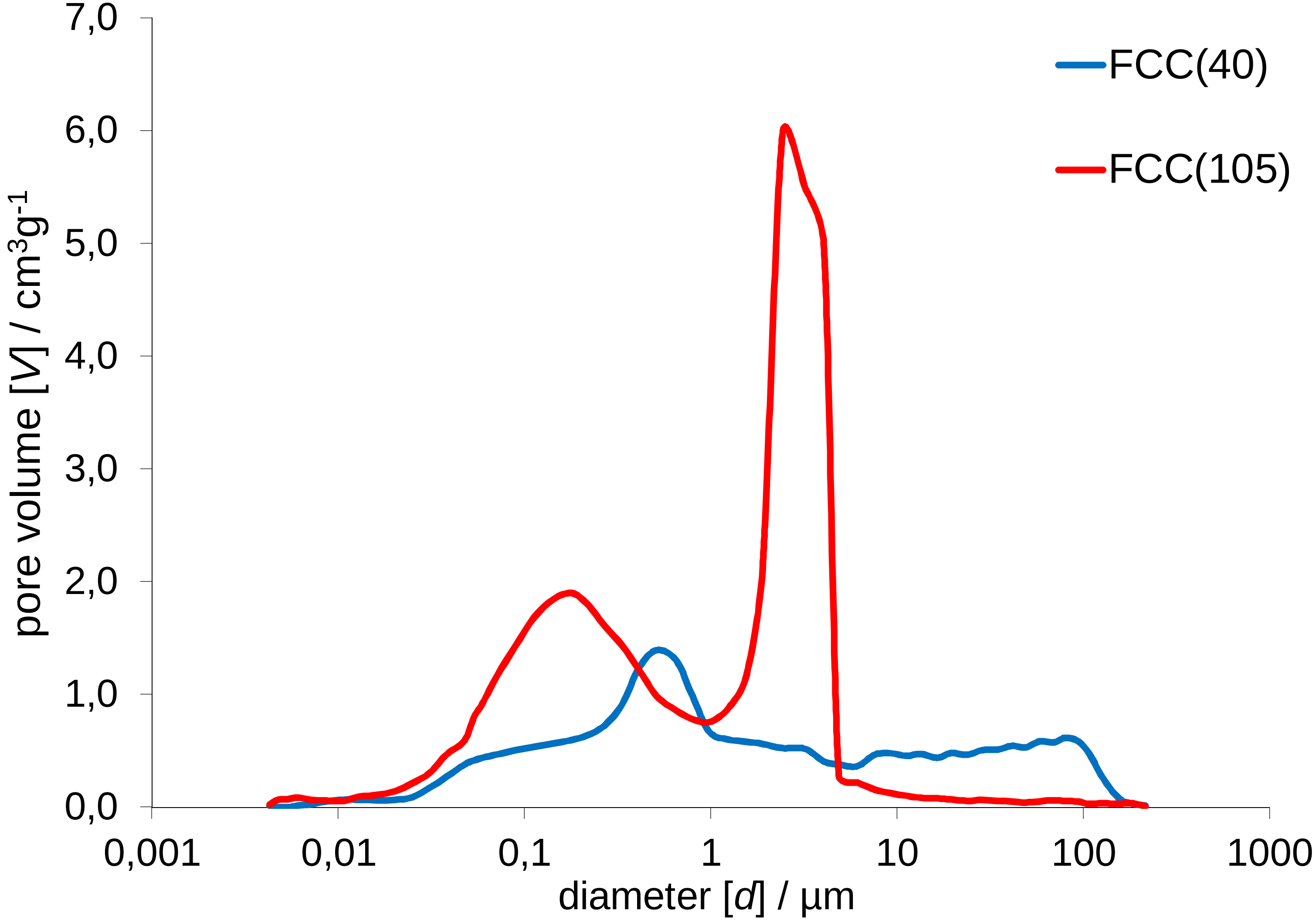
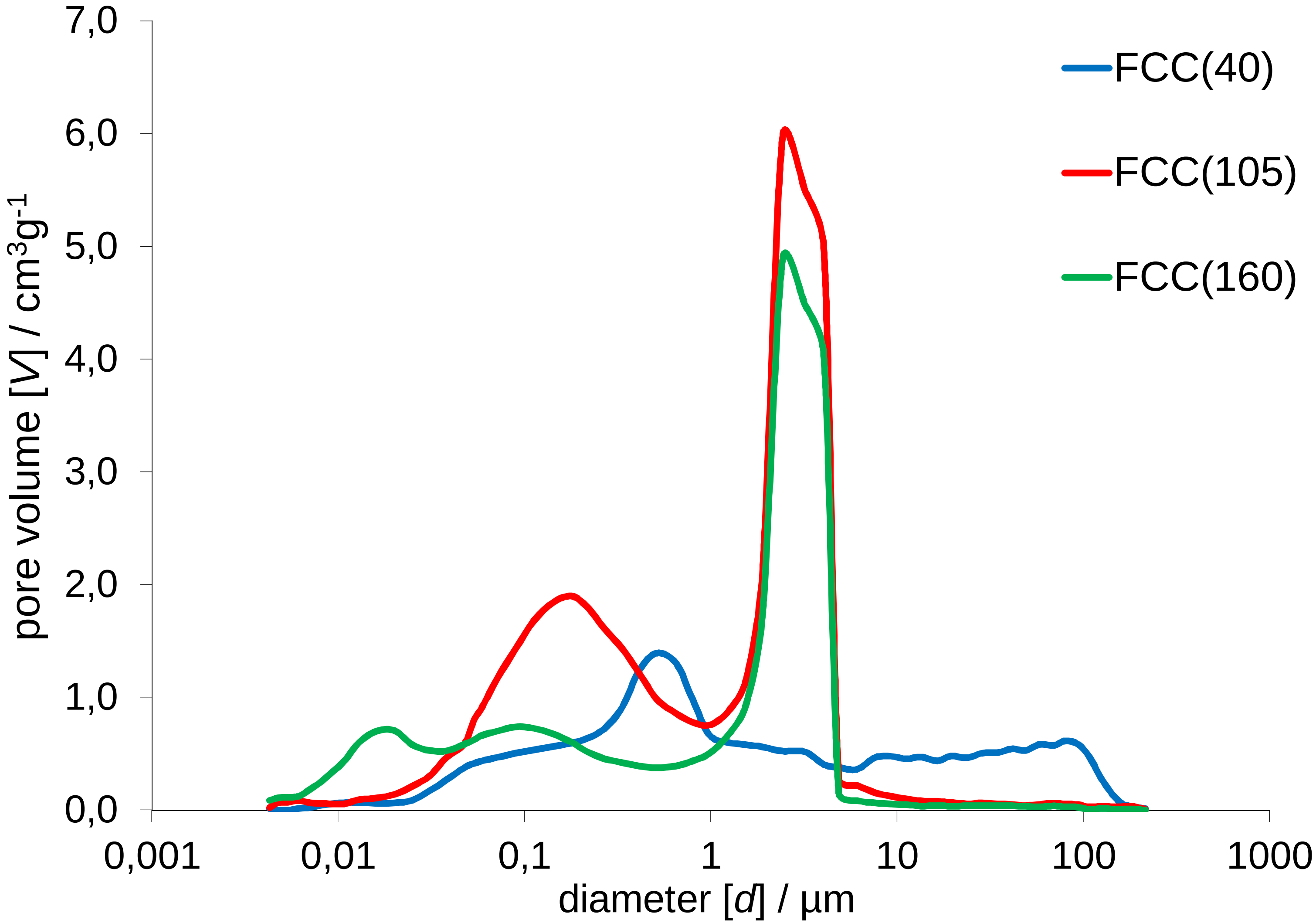


Experimental 2/7:

Pore Size Distribution of Pigments



Experimental 3/7:

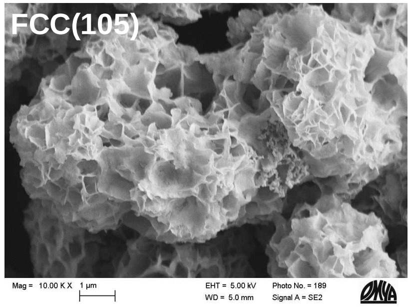
Coating Formulations

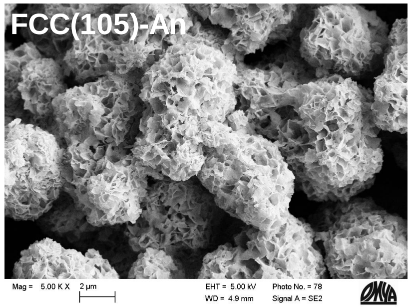
Coating	Specific surface area / m^2g^{-1}	Zeta potential (mV)	Polymer/ Dispersant	Solids content /%	Thickness /µm
FCC(40)	40	-10.7 ± 0.2	-	27.1	51.8 ± 3.8
FCC(105)	105	-12.6 ± 0.2	-	14.7	70.7 ± 3.8
FCC(160)	160	-12.8 ± 0.4	-	18.4	70.6 ± 2.5
FCC(105)-An	105	-22.9 ± 0.2	An (5 pph)	15.5	53.0 ± 8.5
FCC(105)-Cat	105	28.8 ± 1.0	Cat (5 pph)	14.5	63.9 ± 0.8
Silica gel 60 F_{254}	480 - 540	-	-	-	165 - 235

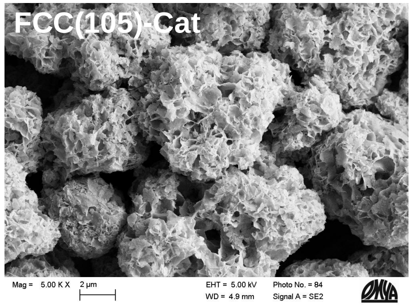
reference TLC plate

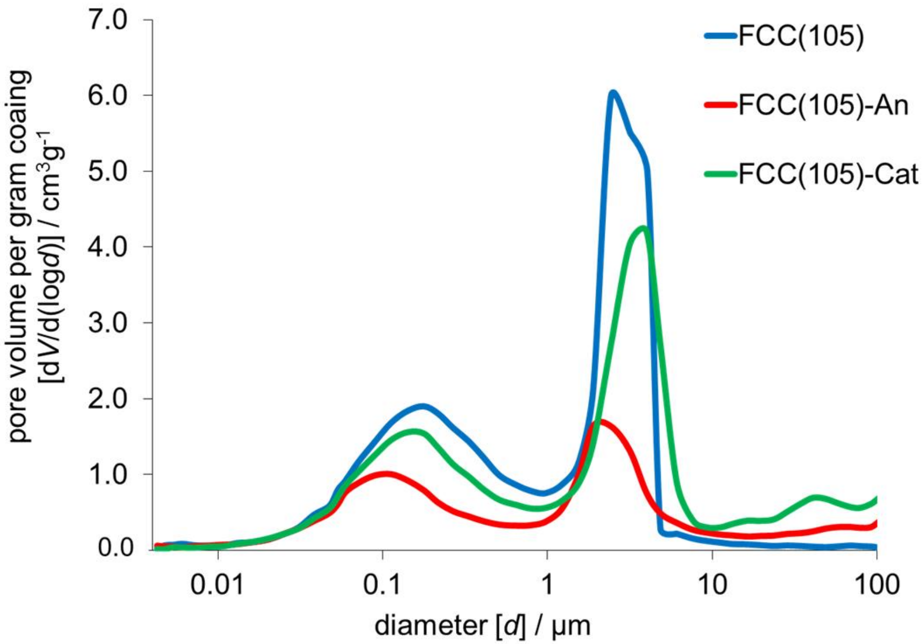
Experimental 4/7:

Impact of Charge Polymer on Pore Volume Distribution









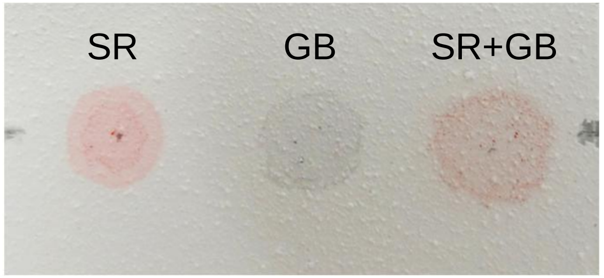
Experimental 5/7:

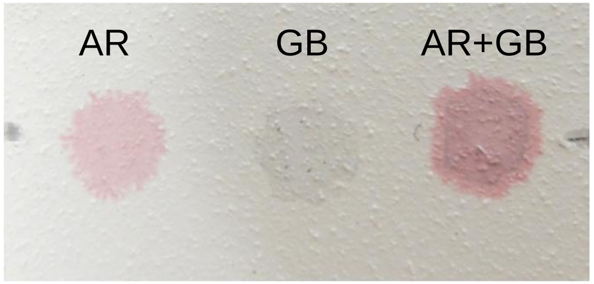
Dyes and Eluents

Dyes:

- 0.1 % Sudan red G in ethanol (SR)
- 0.1 % Amaranth red in deionised water (AR)
- 0.1 % Gardenia blue in deionised water (GB)

Experimental set-up:



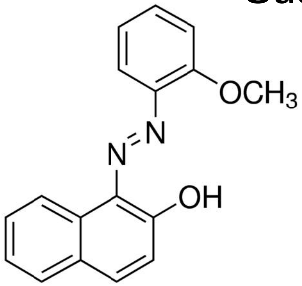


Eluents:

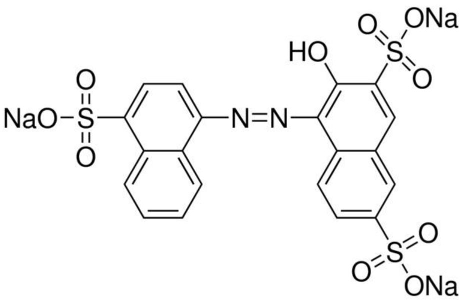
- Denaturated ethanol
- Deionised water

More dyes and eluents will be explored as work continues

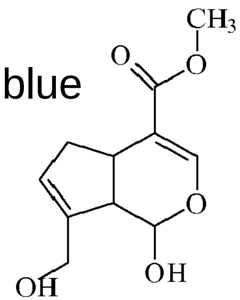
Sudan red



Amaranth red

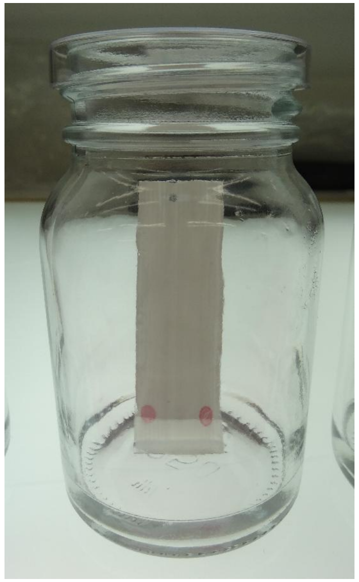


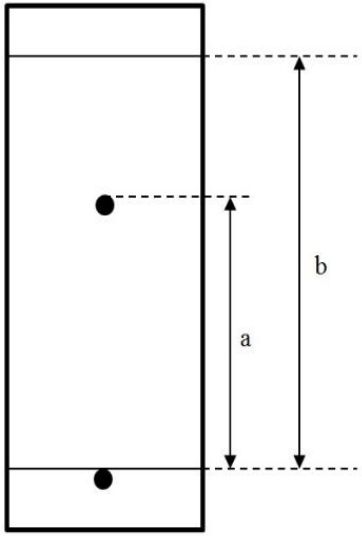
Gardenia blue



Experimental 6/7:
Thin Layer Chromatography (TLC)

- separation of substances into their components
- most common absorbents include silica gel (90 %), modified silica gels, alumina and cellulose
- separation efficiency of an adsorbent is determined by its geometrical structure including surface area, particle and pore size and their respective distributions
- the selectivity depends upon the chemical surface structure of the material





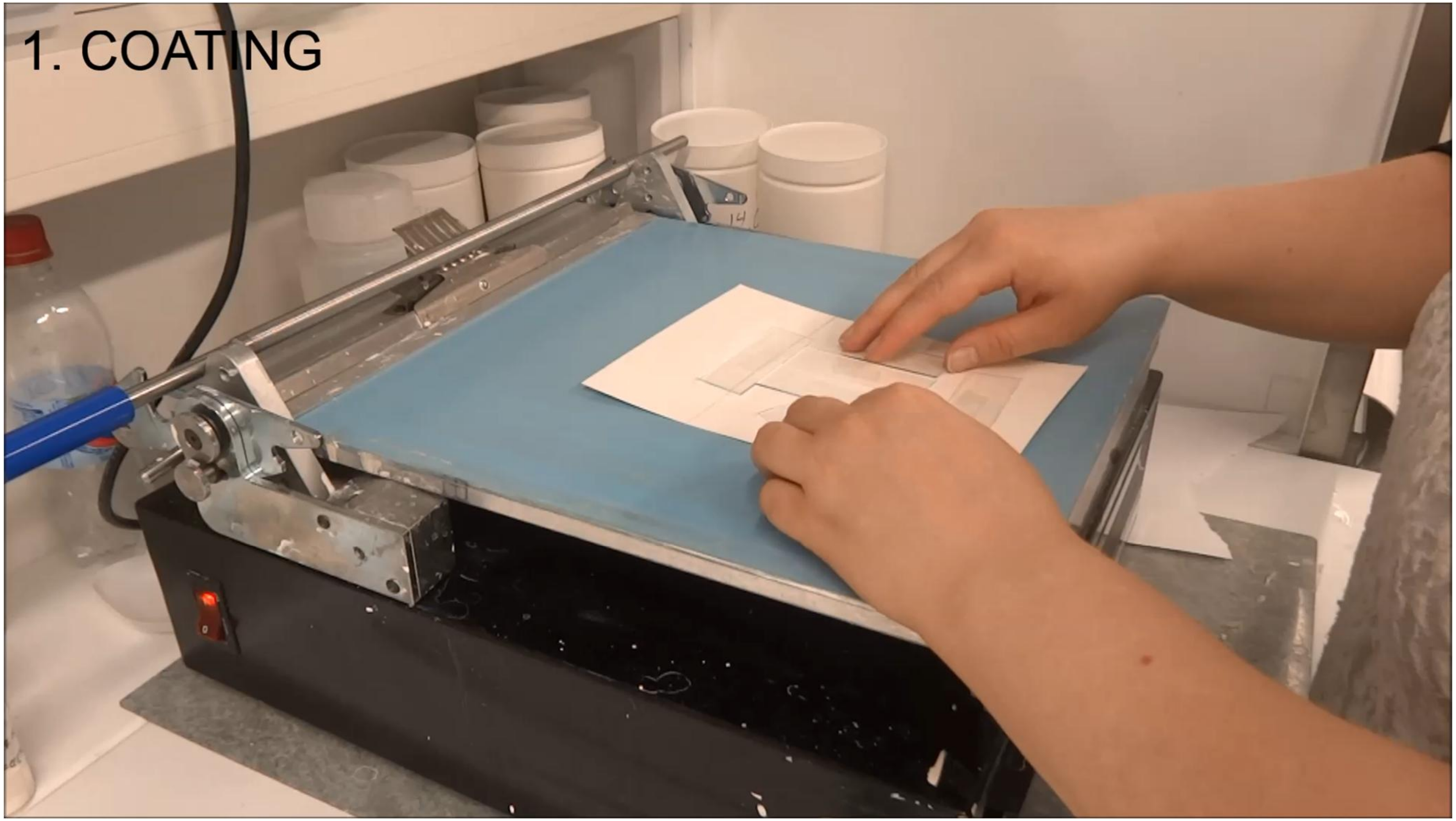
$$R_f = \frac{a}{b}$$

a = distance travelled by the compound

b = distance travelled by the solvent

Experimental 7/7:

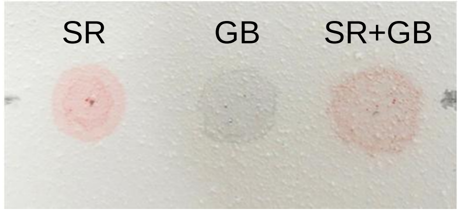
Sample Preparation



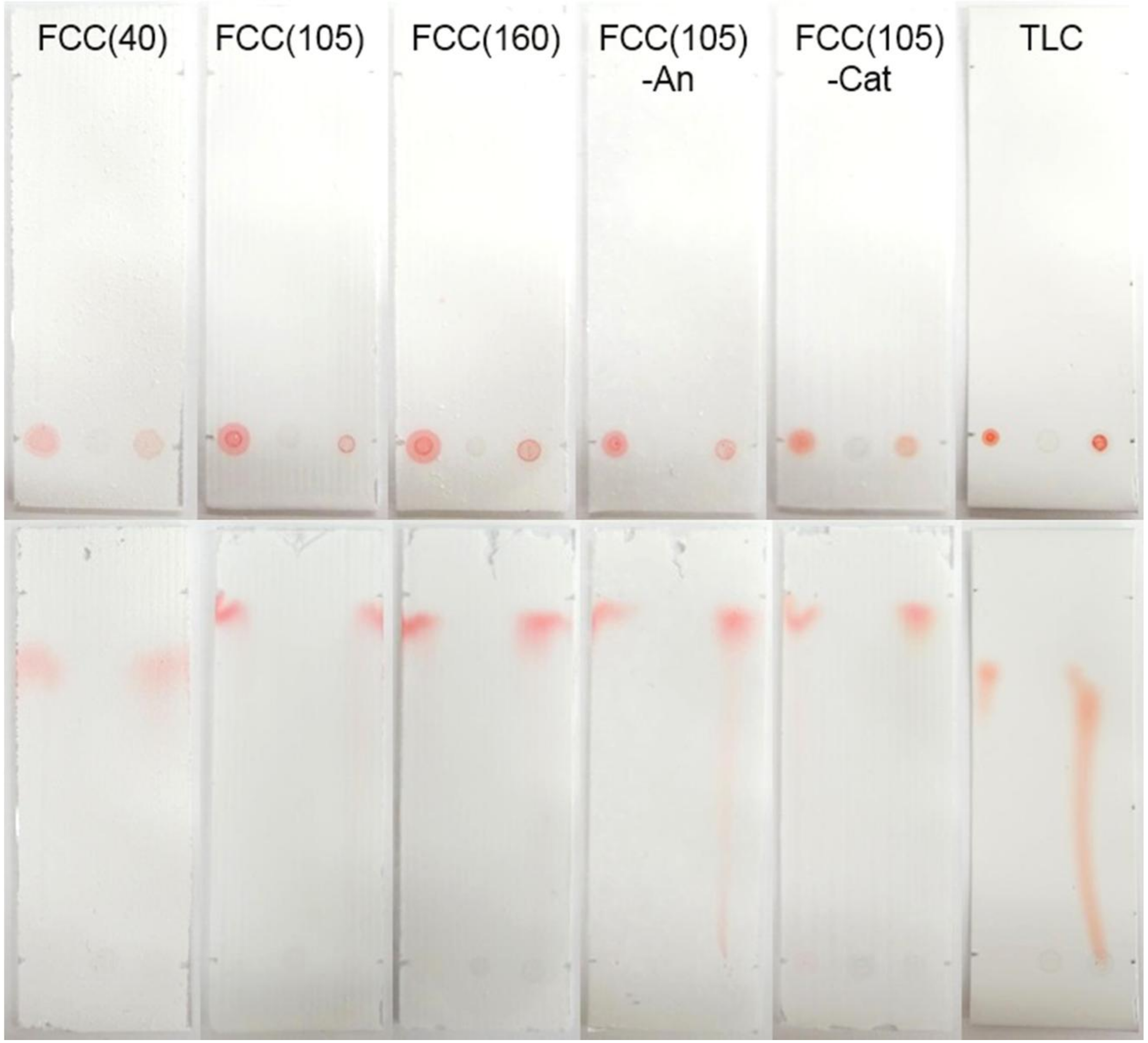
Results

Results 1/4:

Denatured Ethanol as Eluent



Sudan red (SR)
Gardenia blue (GB)

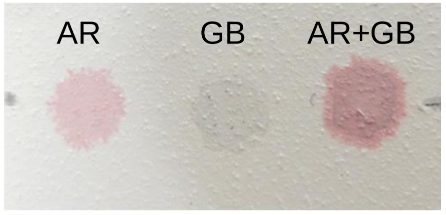


Experimental 2/4:

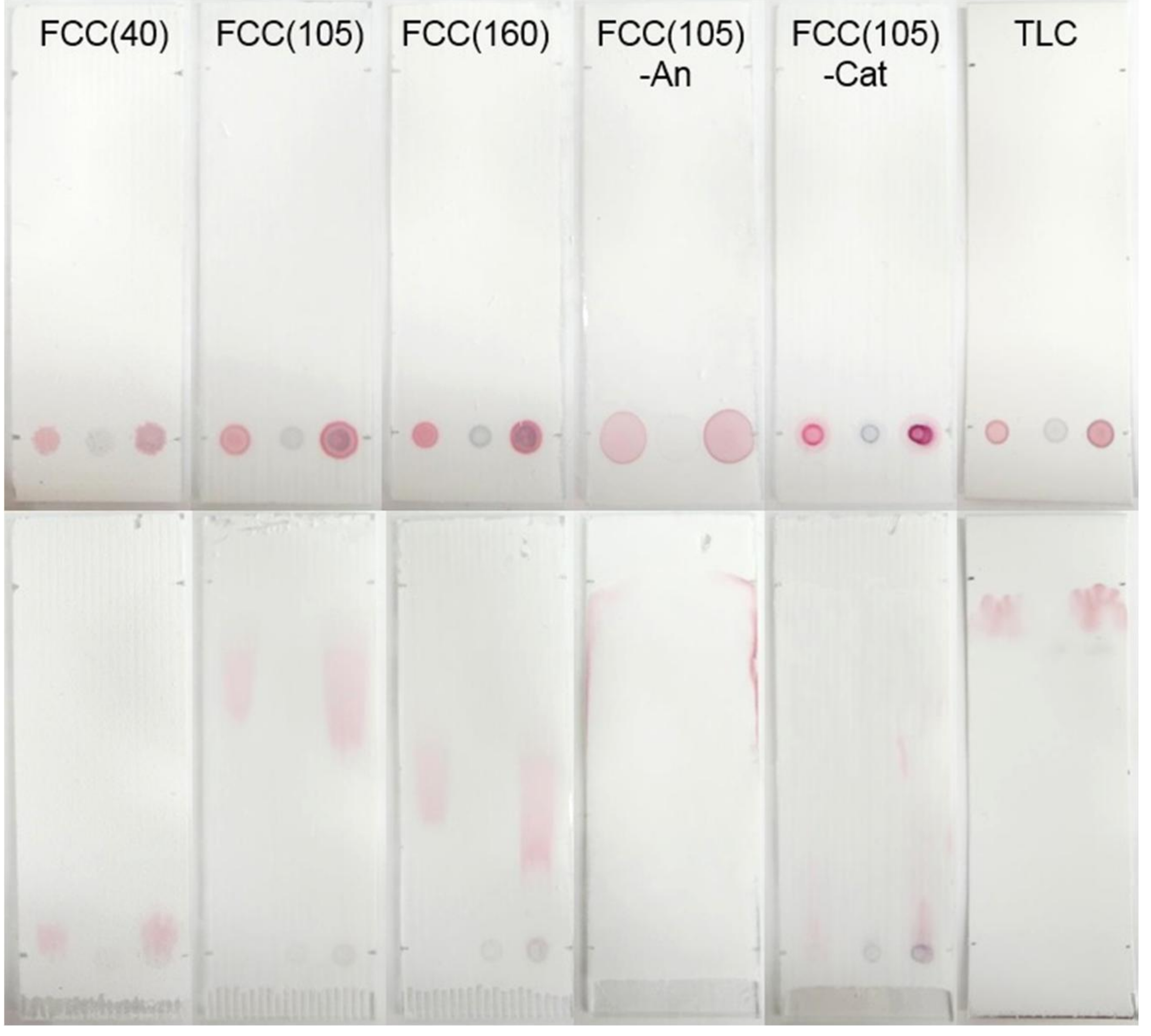
Denatured Ethanol as Eluent

Sample	Solvent front wicking /min	R_f		
		Sudan red in ethanol (0.1 %)	Gardenia blue in water (0.1 %)	Mixture (Sudan red/ Gardenia blue)
FCC(40)	120	0.83	0.00	0.83/0.00
FCC(105)	34	0.95	0.00	0.96/0.00
FCC(160)	33	0.91	0.00	0.93/0.00
FCC(105)-An	43	0.95	0.00	0.95/0.00
FCC(105)-Cat	34	0.96	0.00	0.95/0.00
TLC (silica gel)	20	0.79	0.00	0.80/0.00
Sample	Solvent front wicking /min	Amaranth red in water (0.1 %)	Gardenia blue in water (0.1 %)	Mixture (Amaranth red/ Gardenia blue)
FCC(40)	127	0.00	0.00	0.00/0.00
FCC(105)	27	0.00	0.00	0.00/0.00
FCC(160)	25	0.00	0.00	0.00/0.00
FCC(105)-An	37	0.16	0.00	0.15/0.00
FCC(105)-Cat	30	0.00	0.00	0.00/0.00
TLC (silica gel)	19	0.64	0.00	0.63/0.00

Experimental 3/4:
Deionised Water as Eluent



Amaranth red (AR)
Gardenia blue (GB)



Experimental 4/4:

Deionised Water as Eluent

Sample	Solvent front wicking /min	R_f		
		Sudan red in ethanol (0.1 %)	Gardenia blue in water (0.1 %)	Mixture (Sudan red/ Gardenia blue)
FCC(40)	47	0.00	0.00	0.02/0.02
FCC(105)	10	0.01	0.14	0.02/0.07
FCC(160)	10	0.05	0.14	0.00/0.06
FCC(105)-An	13	0.00	−*	0.00/0.00
FCC(105)-Cat	21	0.00	0.06	0.01/0.04
TLC (silica gel)	77	0.01	0.73	0.00/0.73
Sample	Solvent front wicking /min	Amaranth red in water (0.1 %)	Gardenia blue in water (0.1 %)	Mixture (Amaranth red/ Gardenia blue)
FCC(40)	52	0.07	0.01	0.07/0.01
FCC(105)	11	0.80	0.13	0.80/0.11
FCC(160)	10	0.55	0.08	0.51/0.06
FCC(105)-An	13	0.93	−*	0.92/−*
FCC(105)-Cat	21	0.24	0.06	0.53/0.04
TLC (silica gel)	75	0.93	0.80	0.95/0.79

Conclusions

Conclusions

- Preliminary results show that FCC coatings could potentially be used as a highly wicking and chromatographic medium, and thus suitable for microfluidic diagnostics

  - surface area, pore size and surface charge of the coatings can be used to control the separation of compounds and eluent wicking time, with no evidence of physisorption in the cases studied

  - free cationic polymer in solution leads to coagulation of anionic dyes and resultant size exclusion from the intraparticle pore structure, together with trapping in the interparticle pore space

  - an advantage over prior art paper microfluidics is that only relatively small amounts of analyte need be used due to the high separation spatial resolution capabilities of FCC coatings

- *The introduction of binders, will be further elucidated, with ultimate focus on pharmacy and microfluidic diagnostic applications*

References

Jutila, E., Koivunen, R., Gane, P.A.C., 2015. Effect of coating pigment, binder type and binder amount on planar liquid wicking on coated substrates. Revised and resubmitted for *Journal of Print and Media Technology Research*.

Martinez, A.W., Phillips, S.T., Carrilho, E., Thomas III, S.W., Sindi, H. & Whitesides, G.M. 2008. Simple telemedicine for developing regions: camera phones and paper-based microfluidic devices for real-time, off-site diagnosis. *Analytical Chemistry*, 80(10), pp. 3699-3707.

Ridgway, C.J., Gane, P.A.C. & Schoelkopf, J., 2006. Achieving Rapid Absorption and Extensive Liquid Uptake Capacity in Porous Structures by Decoupling Capillarity and Permeability: Nanoporous Modified Calcium Carbonate. *Transport in Porous Media*, 63, pp. 239-259.

Ridgway, C.J., Kukkamo, V. & Gane, P.A.C. 2011. Effect of Binders and Additives on Inkjet Coating Pigment Pore Structure. PaperCon, *Proceedings of the Tappi Coating and Graphic Arts Conference*, May 2011 Covington Kentucky USA. Tappi Press GA pp. 1305-1319.

Future work

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Thank you!

Acknowledgements

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