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Quantification of Silanol Species on Various Silicas by IR Spectroscopy

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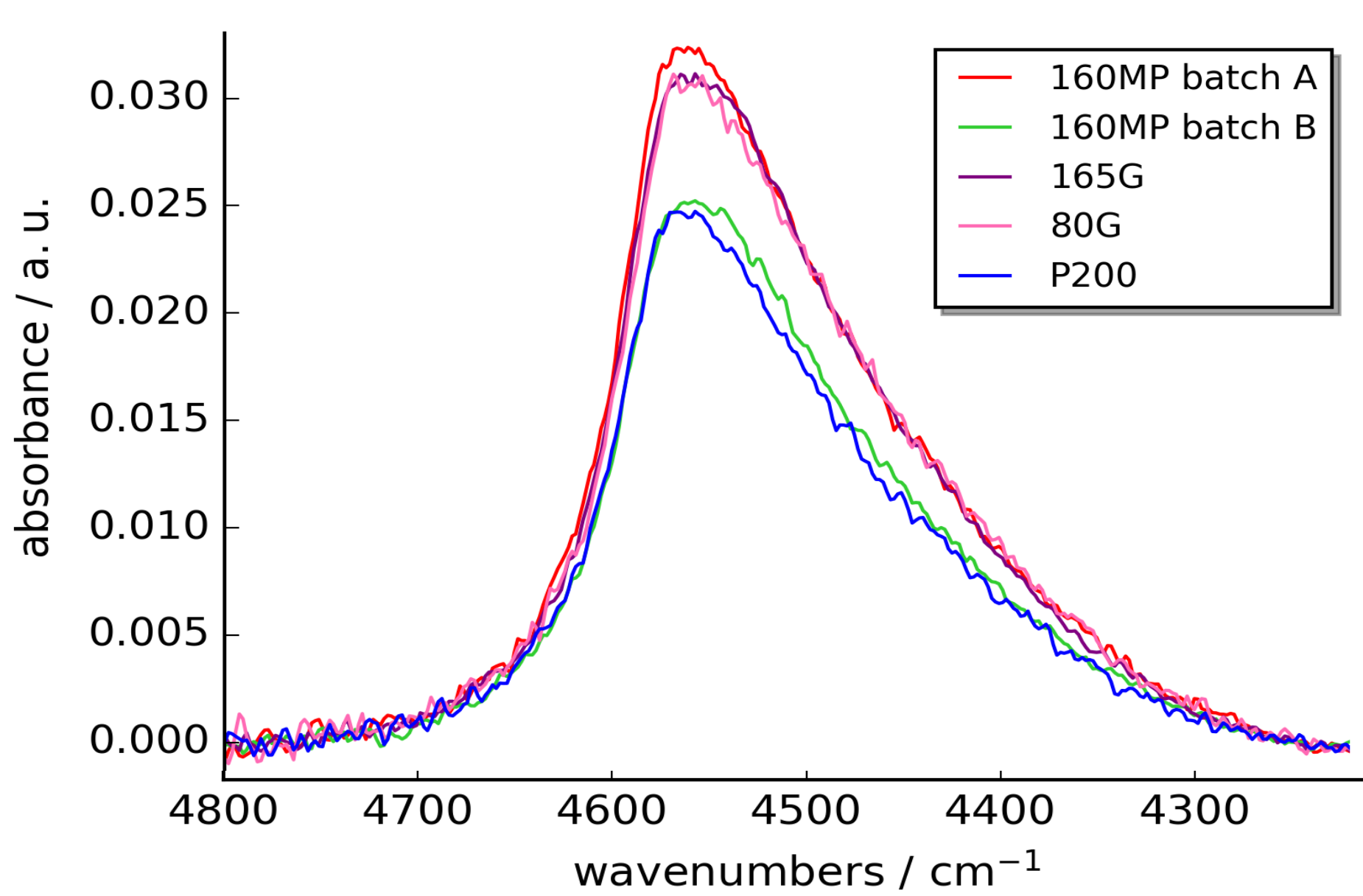
Silica plays a crucial role in the development of Michelin's 'green tyres', which are designed to be more fuel efficient, environmentally friendly, and durable. It is an essential component that reacts with silane, a coupling agent, to significantly improve the tyre's performance. The success of this reaction depends on a thorough understanding of the surface chemistry of silica, in particular the presence of silanol (Si-OH) groups. Silanol groups play an essential role in facilitating chemical bonds between silica, silane, and the tyre polymer matrix. In this study, we embark on a mission to explore the surface reactivity of five distinct silica using *in situ* Fourier transform infrared (FTIR) spectroscopy, following the methodology established by Gallas et al.¹ Beyond qualitative insights, our effort involves quantitative analyses of the surface silanols as a whole, and then of each silanol groups individually. By understanding the reactivity, abundance, and spectral characteristics of these silanol groups, we aim to improve tyre performance by exploiting the full potential of silica-silane interactions.

Silica and probes

- Four commercial silicas are studied using 5 different probes

Silica	Zeosil® 1165MP 1 st	Zeosil® 1165MP 2 nd	Zeosil® Premium	ULTRASIL® 7000GR	ULTRASIL® 4000GR
Sample code	160MP batch A	160MP batch B	P200	165G	80G
Specific surface area (m ² /g)	154,4	154,4	212,4	173	93,9
Probe molecule	Deuterium oxide	methanol	propan-2-ol	2-methyl-propan-2-ol	3-ethyl-pentan-3-ol
Formula	D ₂ O	CH ₄ O	C ₃ H ₈ O	C ₄ H ₁₀ O	C ₇ H ₁₆ O
Structure					
Molecular size (nm)	0,106	0,180	0,276	0,316	0,410

A. Quantification of total number of silanols



$$C_{OH} = \frac{A \cdot S}{\epsilon \cdot m}$$

C_{OH} : Concentration of silanols (mol g⁻¹)
 A : area of the $(\nu + \delta)(OH)$ band (cm⁻¹)
 S : pellet's geometrical surface (2.01 cm²)
 ϵ : molar absorption coefficient (cm mol⁻¹)
 m : Pellet's mass (g)

	160MP batch A	160MP batch B	165G	80G	P200
C_{OH} (mmol/g)	3.6	3.0	3.3	3.2	3.0

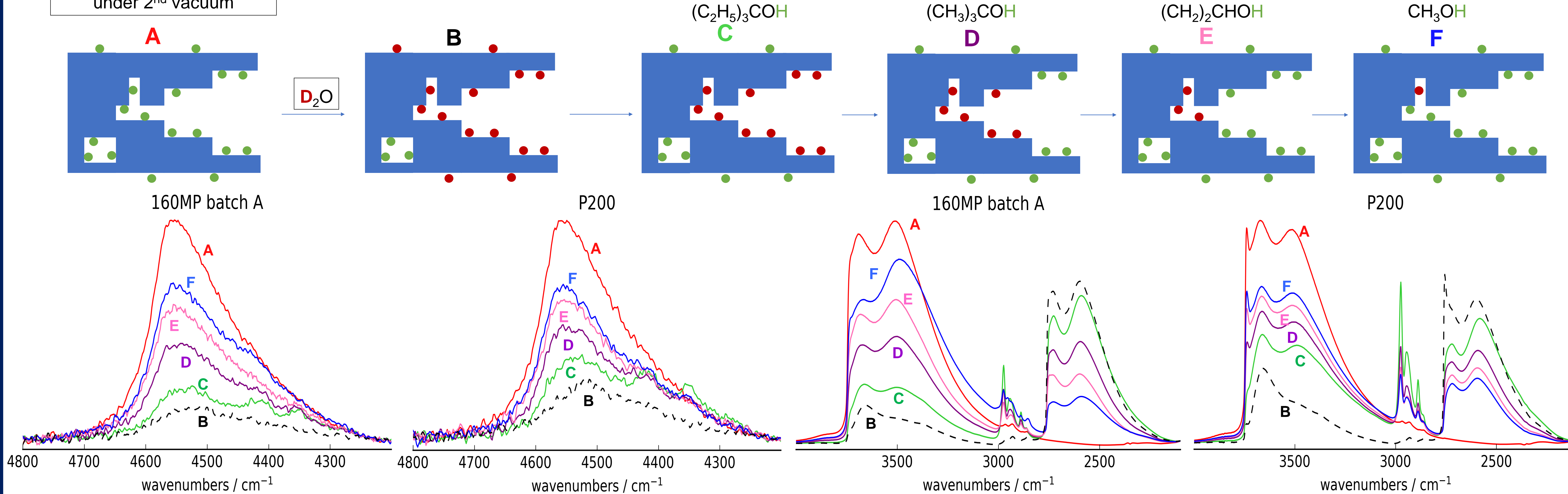
B. Assessment of silanols accessibility

- in situ* FTIR measures (under vacuum) qualitatively and quantitatively surface properties of catalysts by probe molecule
- H-D/O-D exchange and retro exchange

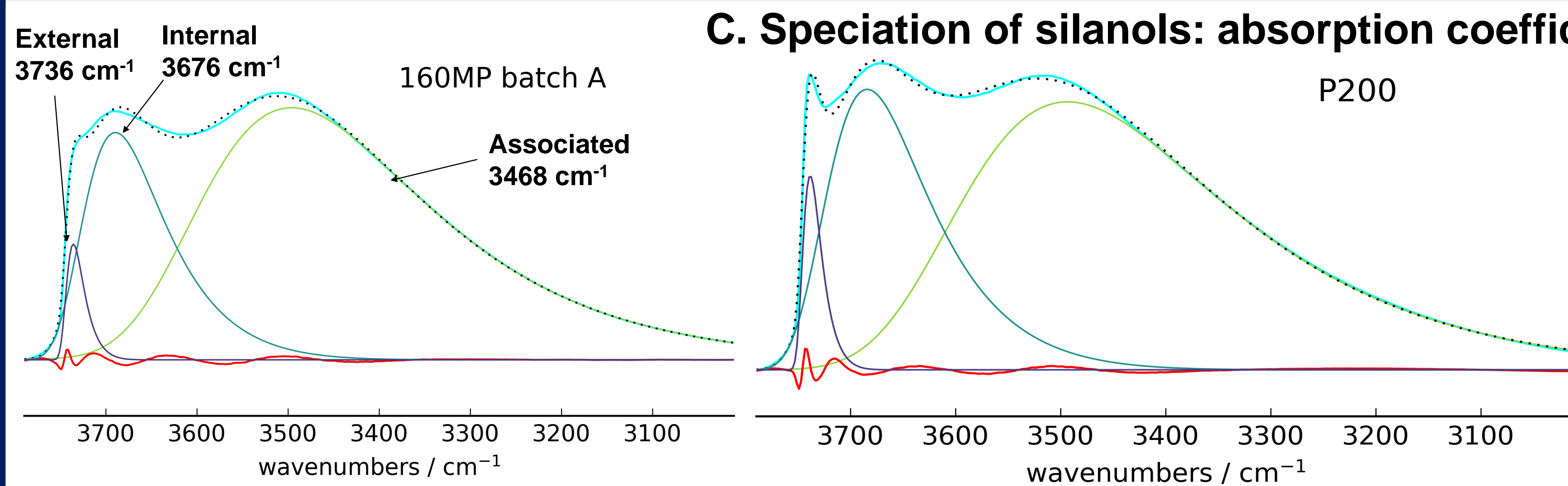
1. Activation overnight under 2nd vacuum

2. Exchange with D₂O

3. Retro-exchange with 4 alcohols from larger to smaller size.



C. Speciation of silanols: absorption coefficients and quantification



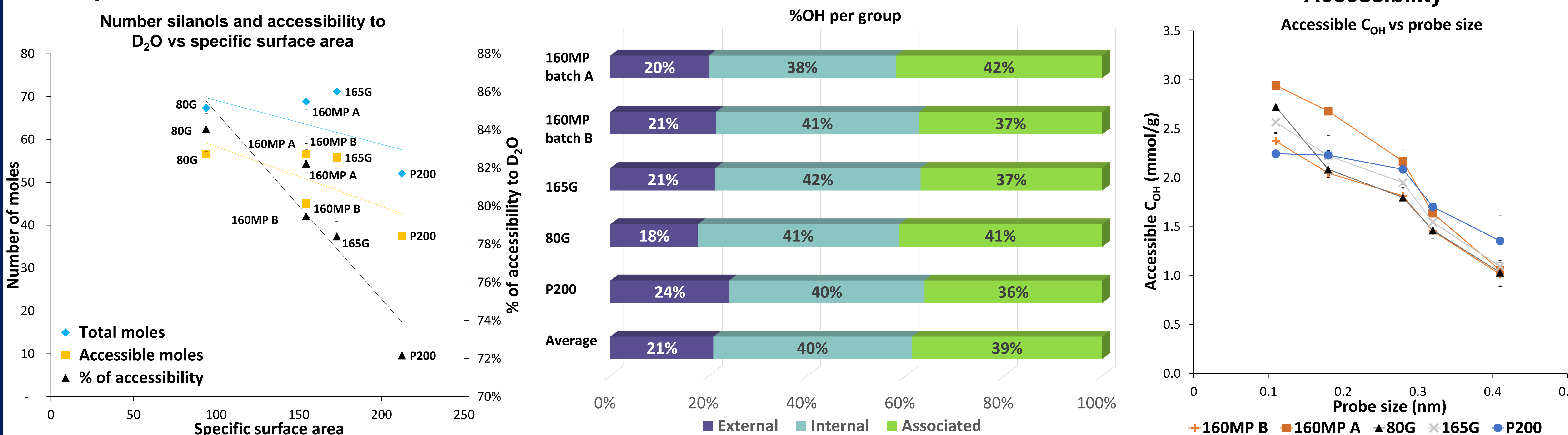
Assuming ϵ_i are independent of the samples (A, B, ...G), the following linear system holds:

$$\begin{pmatrix} m_A \times C_{OH_A}/S \\ \vdots \\ m_G \times C_{OH_G}/S \end{pmatrix} = \begin{pmatrix} A_{ext_A} & A_{int_A} & A_{ass_A} \\ \vdots & \ddots & \vdots \\ A_{ext_G} & A_{int_G} & A_{ass_G} \end{pmatrix} \begin{pmatrix} \epsilon_{ext}^{-1} \\ \epsilon_{int}^{-1} \\ \epsilon_{ass}^{-1} \end{pmatrix}$$

Its resolution yields:

- ϵ_{ext} = 1.57 +/- 0.42 cm/μmol
- ϵ_{int} = 7.37 +/- 1.31 cm/μmol
- ϵ_{ass} = 20.0 +/- 2.04 cm/μmol

D. Comparison of commercial silicas



Conclusion

- No correlation of the total number of OH groups with BET or CTAB surface area
- Consistent absorption coefficients ϵ , correlated with the extent of hydrogen bonding
- No significant variation in the distribution of external, internal, and accessible silanol groups among the various silica samples.
- Slight changes in accessibility, only significant for two samples (160MP batch A vs. P200)

¹J.-P. Gallas, J.-M. Goupil, A. Vimont, J.-C. Lavalley, B. Gil, J.-P. Gilson and O. Miserque, Langmuir, 25, 5825–5834 (2009).