

ELECTRONIC SUPPLEMENTARY INFORMATION

CHITOSAN-MODIFIED COTTON THREAD FOR THE PRECONCENTRATION AND COLORIMETRIC TRACE DETERMINATION OF Co(II)

Willian Toito Suarez,¹ Mathews O. K. Franco,¹ Luis Fermín Capitán-Vallvey,^{2,3} Miguel M. Erenas^{*2,3}

¹Department of Chemistry, Centre for Exact Sciences and Technology, 36570-900, Federal University of Viçosa, Viçosa - MG, Brazil. ²Department of Analytical Chemistry.

³Unit of Excellence in Chemistry applied to Biomedicine and the Environment, University of Granada. Campus Fuentenueva, Faculty of Sciences, 18071, University of Granada, Spain.

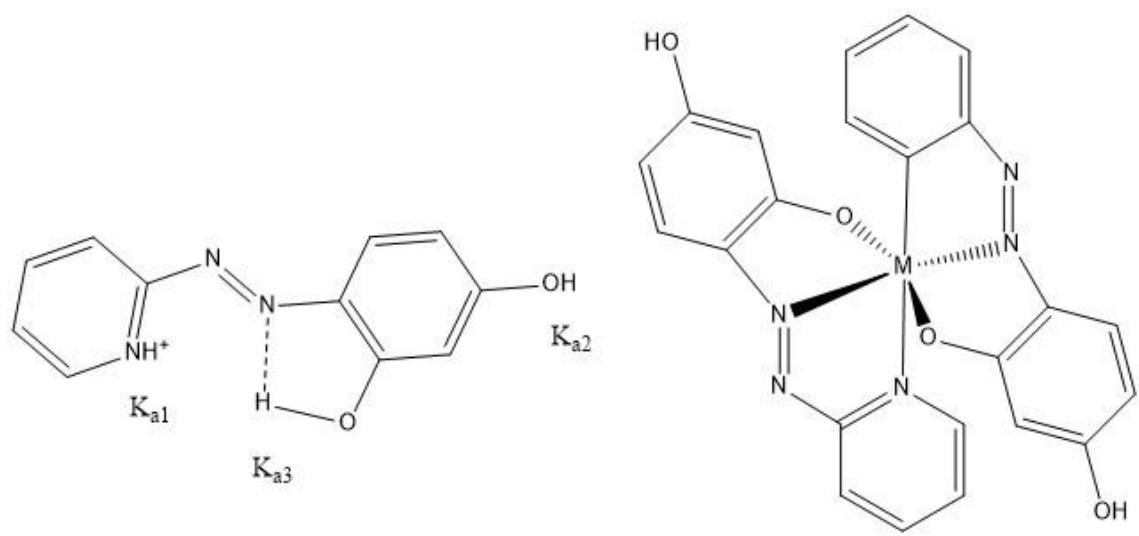


Figure S1. 4-(2-pyridylazo) resorcinol (PAR) molecule (left) and PAR complex (right).

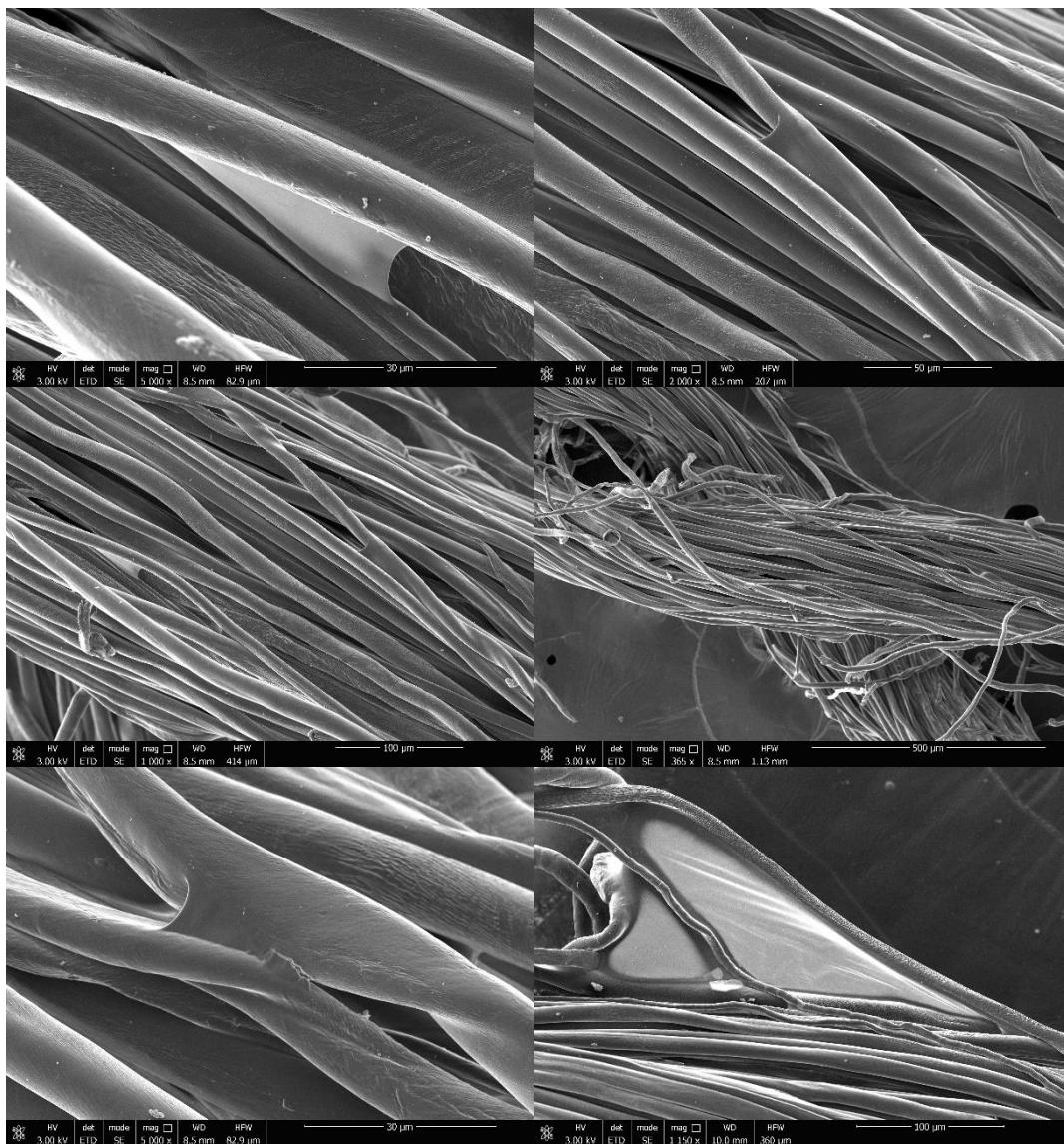


Figure S2. Different images of μ TAD sensing zone containing chitosan. Obtained with FEG-ESEM, QuenScan 650F FEI[®] electronic microscope together with an Everhart–Thornley detector (ETD), circular backscatter detector (CBS) and energy-dispersive detector (EDS). From Centre for Scientific Instrumentation, University of Granada, Spain.

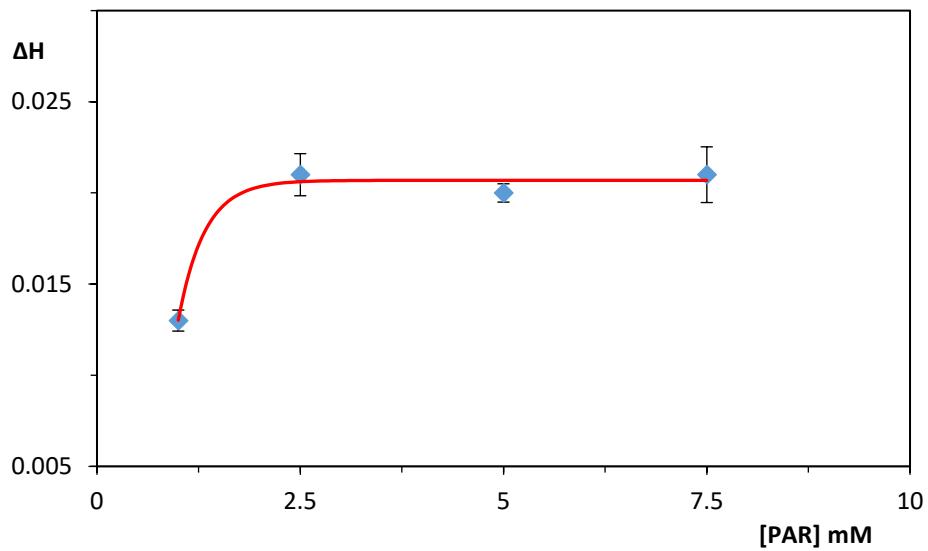


Figure S3. Study of the influence of PAR concentration on ΔH ($H_{\text{PAR}} - H_{\text{PAR-Co}}$).

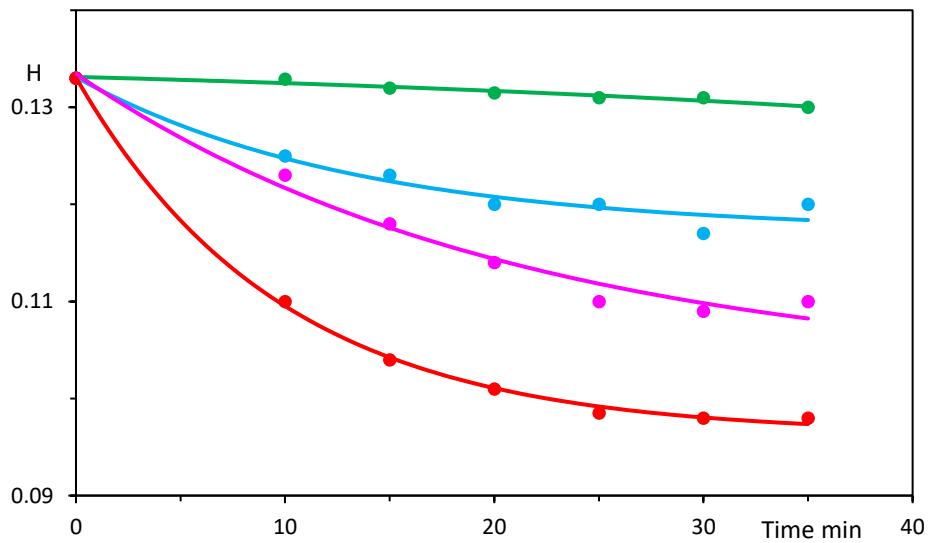


Figure S4. Evolution of H with time at different Co(II) concentrations: 50 $\mu\text{g}\cdot\text{L}^{-1}$ (green data), 100 $\mu\text{g}\cdot\text{L}^{-1}$ (blue data), 150 $\mu\text{g}\cdot\text{L}^{-1}$ (magenta data) and 200 $\mu\text{g}\cdot\text{L}^{-1}$ (red data).

Table S1. Determination of Co(II) in spiked water samples using Atomic Absorption Spectrometry (AAS) as reference method (n=3)

Sample	Found ($\mu\text{g}\cdot\text{L}^{-1}$)	Added ($\mu\text{g}\cdot\text{L}^{-1}$)	μTAD ($\mu\text{g}\cdot\text{L}^{-1}$)	AAS ($\mu\text{g}\cdot\text{L}^{-1}$)	Error (%)
Tap water	<6.5	50	52±2	49.2± 0.3	5.7
	<6.5	100	99±2	101.0±0.5	2.0
	<6.5	150	155±3	152.0±0.1	1.7
	<6.5	200	208±2	199.5±0.2	4.3
	<6.5	250	262±3	248.9±0.2	5.3
	<6.5	300	288±3	301.2±0.4	4.4

Table S2. Figures of merit of microfluidic devices for Co(II) determination in water.

Substrate	Linear Range	LOD	Reference
Paper	Qualitative	50 μM	[1]
Paper	Semiquantitative	0.5 $\mu\text{g}\cdot\text{L}^{-1}$	[2]
Paper	$590 - 5.9 \times 10^5 \mu\text{g}\cdot\text{L}^{-1}$	$58.9 \mu\text{g}\cdot\text{L}^{-1}$	[3]
Paper	$500 - 2000 \mu\text{g}\cdot\text{L}^{-1}$	$590 \mu\text{g}\cdot\text{L}^{-1}$	[4]
Paper	10-1000 μM	1 μM	[5]
Thread	$25 - 600 \mu\text{g}\cdot\text{L}^{-1}$	$6.50 \mu\text{g}\cdot\text{L}^{-1}$	This work

- [1] L. Feng, X. Li, H. Li, W. Yang, L. Chen, Y. Guan, Enhancement of sensitivity of paper-based sensor array for the identification of heavy-metal ions, *Analytica Chimica Acta*, 780 (2013) 74–80.
- [2] L.H. Mujawar, A.A. Felemban, M.S. El-Shahawi, Hexamethyldisilazane modified paper as an ultra-sensitive platform for visual detection of Hg^{2+} , Co^{2+} , Zn^{2+} and the application to semi-quantitative determination of Hg^{2+} in wastewater, *Analytical Sciences*, 32 (2016) 491–497.
- [3] M. Rahbar, P.N. Nesterenko, B. Paull, M. Macka, Geometrical Alignment of Multiple Fabrication Steps for Rapid Prototyping of Microfluidic Paper-Based Analytical Devices, *Analytical Chemistry*, 89 (2017) 11918–11923.
- [4] K.R. Chabaud, J.L. Thomas, M.N. Torres, S. Oliveira, B.R. McCord, Simultaneous colorimetric detection of metallic salts contained in low explosives residue using a microfluidic paper-based analytical device (μ PAD), *Forensic Chemistry*, 9 (2018) 35–41.
- [5] L.H. Mujawar, M.S. El-Shahawi, Poly(methyl methacrylate)-modified cellulose fibers patterned with highly selective chromogenic reagent for rapid and trace determination of Co^{2+} in water, *Analytical Methods*, 10 (2018) 4454–4462.