

Supporting information for

Sulphate-selective optical microsensors: overcoming the hydration energy penalty[†]

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Experimental section

Reagents: Latex beads (polystyrene, 0.8 μm mean particle size, without azide), 1,3-[Bis(3-phenylthioureidomethyl)]benzene (sulfate ionophore I, Selectophore), tridodecylmethylammonium chloride (TDMACl, Selectophore), tetrahydrofuran (THF, anhydrous 99.9 %), magnesium acetate tetrahydrate (99% purity); analytical grade sodium salts of sulfate, thiocyanate, chloride, bromide, lactate, salicylate and nitrate were all purchased from Sigma-Aldrich (Spain). Acetic acid (96% purity) was obtained from Riedel-de Haën (Germany). Doubly distilled deionized water ($18.1 \text{ M}\Omega\cdot\text{cm}^{-1}$ resistance) was produced by a Milli-Q water system (Millipore Corporation, Bedford, MA). The chromoionophore fluorescein octadecyl ether was synthesized according to a previous report.¹

SO_4^{2-} -selective polystyrene microspheres: Preparation.

1. THF cocktail

Stock solutions of 10 mM of the chromoionophore, 10 mM of sulfate ionophore I and 10 mM of TDMACl in THF were firstly prepared. 300 μl of the chromoionophore, 300 μl of sulfate ionophore I, 270 μl of TDMACl and 130 μl of THF were mixed to obtain a final solution of 1 ml THF (3 mM Chromoionophore, 2.7 mM TDMACl and 3 mM sulphate ionophore I).

2. Sensing polystyrene beads

10 μl of latex beads (polystyrene) were diluted to 40 mL of H_2O . 0.5 mL of the THF cocktail were pipetted and mixed with 4.5 mL of the diluted PS microspheres suspension on a vortex with a spinning speed of 1200 rpm. The yellow suspension is then blown with compressed N_2 for 20 min to remove THF.

SO_4^{2-} -selective polystyrene microspheres: System and measurements.

The system works in exhaustive sensing mode by mixing the PS beads prepared previously with a 30 mM acetic acid/magnesium acetate buffer at pH 4 in a ratio of 2:1 of PS and buffer respectively, thus a final concentration of 10 mM of buffer will be obtained in the system. Calibration curves were recorded by gradual addition of Na_2SO_4 or other salt stock solutions.

Instrumentation.

Absorbance measurements were carried out in a 8453 UV-Vis spectrophotometer from Agilent Technologies (Barcelona, SPAIN) with an OS High Precision Cell optical glass cuvette of 10 mm light path (Hellma Analytics, Germany). pH values were obtained with a pH meter GLP 21 from CRISON (Alella, Barcelona).

Table S1. Values of concentration of each compound in the THF cocktail to find the most selective composition.

<i>Chromoionophore</i> (mM)	<i>TDMACl</i> (mM)	<i>Sulfate ionophore</i> (mM)	<i>Abs SO₄²⁻</i> <i>/ Abs Cl-</i>	<i>Abs SO₄²⁻ /</i> <i>Abs SCN-</i>
2.0	1.6	-	5.15	1.15
1.6	2.0	-	5.02	1.52
3.0	2.7	-	3.01	2.04
2.7	3.0	-	3.56	1.78
4.0	3.6	-	2.94	1.73
3.6	4.0	-	3.72	1.75
3.0	2.7	3	4.29	2.48

Table S2. Results of all the samples predicted with additional amounts of known SO_4^{2-} concentrations predicted for validation of the system, and the recoveries obtained for each concentration.

Biological range	<i>4.1 – 29.1 mM²</i>	
Sample 1	<i>8.4 ± 0.3 mM</i>	
Added (μM)	Predicted (μM)	Recovery (%)
3.9	4.0 ± 0.2	97 ± 4
4.8	4.9 ± 0.1	99 ± 3
5.8	5.8 ± 0.1	100 ± 3
6.8	6.8 ± 0.2	100 ± 4
7.6	7.8 ± 0.5	102 ± 7
Sample 2	<i>9.5 ± 0.6 mM</i>	
Added (μM)	Predicted (μM)	Recovery (%)
5.7	5.7 ± 0.1	98 ± 3
6.7	6.6 ± 0.1	100 ± 2
7.6	7.5 ± 0.3	101 ± 5
8.6	8.4 ± 0.2	103 ± 3
9.5	9.1 ± 0.3	105 ± 6
Sample 3	<i>20.0 ± 0.1 mM</i>	
Added (μM)	Predicted (μM)	Recovery (%)
11.0	10.8 ± 0.3	101 ± 4
11.9	11.7 ± 0.4	102 ± 6
12.8	12.6 ± 0.2	102 ± 3
13.9	13.5 ± 0.2	103 ± 4
14.9	14.5 ± 0.5	102 ± 8
Sample 4	<i>11.9 ± 0.2 mM</i>	
Added (μM)	Predicted (μM)	Recovery (%)
6.9	6.9 ± 0.1	99 ± 2
7.9	7.9 ± 0.1	100 ± 3
8.9	8.7 ± 0.3	102 ± 5
9.8	9.5 ± 0.2	104 ± 3
10.8	10.4 ± 0.3	105 ± 4
Sample 5	<i>8.2 ± 0.6 mM</i>	
Added (μM)	Predicted (μM)	Recovery (%)
4.3	4.4 ± 0.3	99 ± 5
5.3	5.4 ± 0.2	98 ± 3
6.3	6.2 ± 0.1	101 ± 2
7.3	7.0 ± 0.5	104 ± 6
8.3	7.9 ± 0.2	105 ± 4

² Appel, L. J. In *Dietary reference intakes for water, sodium, potassium, chloride and sulfate*. The National Academies Press, **2005**; pp. 424 – 448.

Fig. S1. Up: Calibration curves for a SO_4^{2-} -selective PS microspheres with the difference in absorbance at 459 nm ($A_0 - A$) against SO_4^{2-} and other interfering anions. Down: Calibration curves for a PS microspheres optical system (without sulphate ionophore) with the difference in absorbance at 459 nm ($A_0 - A$) against SO_4^{2-} and other interfering anions.

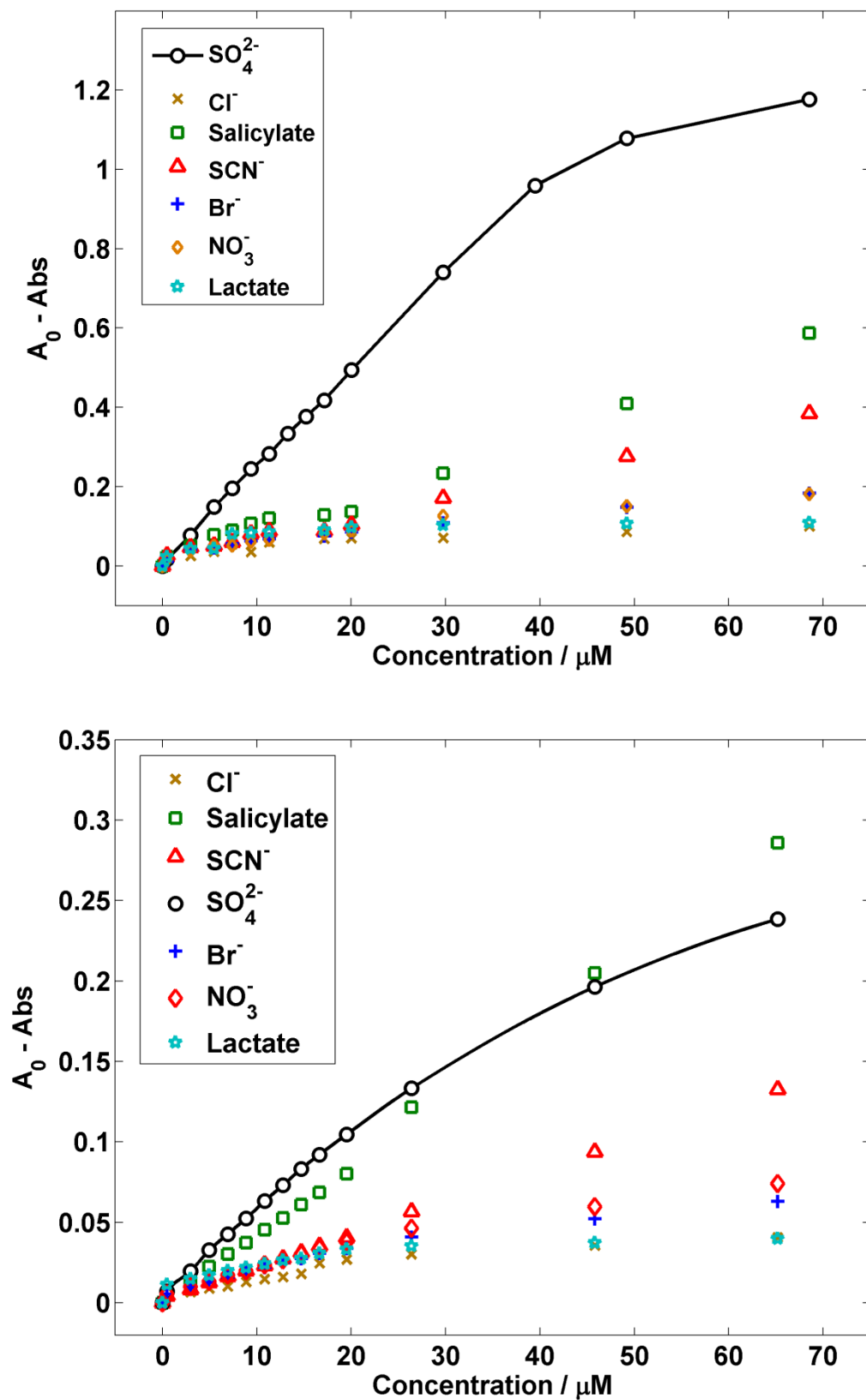


Fig. S2. Up: Spectra of the sulphate sensor in 10 mM HAc/MgAc at pH 4 upon an initial addition of SO_4^{2-} and successive additions of Cl^- . Down: The first two points show the initial absorbance (A_0) at 459 nm and the change observed after the addition of SO_4^{2-} (25 μM) in the absence of Cl^- . Then, the graph displays the changes in absorbance for a solution with constant concentration of SO_4^{2-} (25 μM) upon the addition of increasing concentrations of Cl^- .

