Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

A simple fluorescence assay for the detection of fluoride in water at neutral pH

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1. General : All reagents were commercially available and used as received: $CaCl_2$ x $2H_2O$, NaF, NaBr, NaI, CH_3COONa x 3 H_2O, $NaClO_4$ x H_2O, NaCN, Na_2CO_3, $NaNO_2$, $NaNO_3$, NaSCN, Na_2HPO_4, $Na_2H_2P_2O_7$, MOPS (Fluka), NaCl, CaF_2 (Acros), NaN_3, Na_2SO_4, BAPTA (Sigma-Aldrich). MOPS buffer (100 mM) was prepared with bidistilled H_2O and used for all experiments (the pH was adjusted to 7.0 by titration with KOH). Stock solution of calcium chloride (5.0 mM) and of BAPTA (2.5 mM) were prepared in 100 mM MOPS buffer. The BAPTA solution was stored at 4 °C and renewed after 1 week. Stock solutions of the sodium salts (10 or 100 mM) were prepared in bidistilled water. Toothpastes (Beverly Hills Formula© (BHF), Elmex© Green, Elmex© for kids, Meridol©, Signal© for kids) and mouthwashes (Colgate©, Elmex© Red, Meridol©) were purchased from local stores. Fluorescence measurements were recorded at 25 °C on a Varian Cary Eclipse spectrophotometer.

2. Procedure for the detection of fluoride in water :

Step 1 : Stock solutions of $CaCl_2$ in MOPS buffer (1.0 mL) and NaF in water (appropriate volume to obtain the desired $[F^-]$ concentration) are mixed, and the volume is completed to 2.0 mL with bidistilled water. The concentrations are $[Ca^{2+}]$ = 2.5 mM, [MOPS] = 50.0 mM, and $[F^-]$ depends on the volume of NaF that was added. Solid CaF_2 (10 mg) is added to initiate precipitation, the mixture is vigorously shaken, and left to equilibrate at room temperature for at least 2 hours.

Step 2 : The solution is filtered through a 0.2 µM membrane filter (Exapure™). An aliquot (1.0 mL) is poured into 1.0 mL of the BAPTA stock solution in MOPS. The mixture is immediately ready for fluorescence measurements (λ_{ex} = 316 nm). The final concentrations are [BAPTA] = 1.25 mM, [MOPS] = 75.0 mM, $[Ca^{2+}] \leq 1.25$ mM.

The fluorescence spectra obtained with different quantities of NaF stock solution added in *Step 1* are shown in Fig. S1 and Fig. 1. The results shown in Fig. 1 are used as calibration curve to determine fluoride content of dental care products (see points 3 and 4).

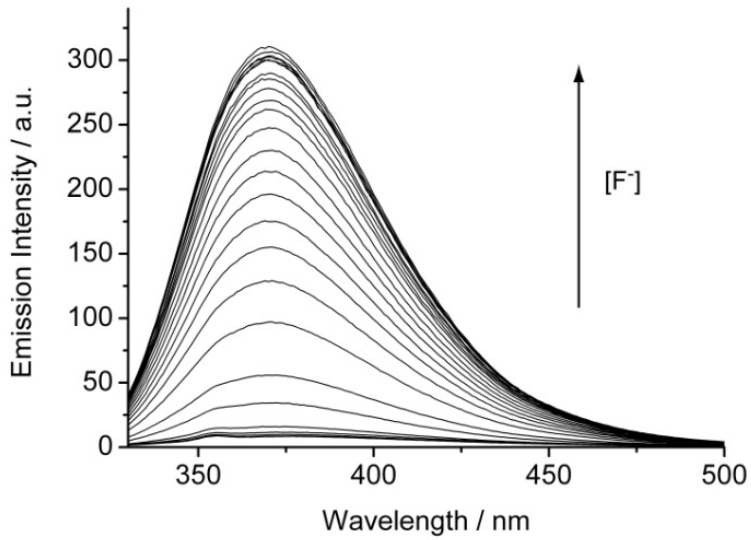

Fig. S1 Fluorescence emission spectra (λ_{ex} = 316 nm) for solutions containing different amounts of fluoride. The assays were performed as described in the main text. The data were obtained at 25 °C in H_2O (pH 7.0, 75 mM MOPS buffer). The curves represent averages of three independent measurements.

3. Procedure for the detection of various anions in water :

Step 1 : Stock solutions of $CaCl_2$ in MOPS buffer (1.0 mL) and Na_nX in water (100 µL) are mixed, and the volume is completed to 2.0 mL with bidistilled water. The concentrations are $[Ca^{2+}]$ = 2.5 mM, [MOPS] = 50.0 mM, and $[X^{n-}]$ = 5.0 mM. Solid CaF_2 (10 mg) is added, the mixture is vigorously shaken, and left to equilibrate at room temperature for at least 2 hours.

Step 2 : Performed in the same way as in point 2.

4. Procedure for the detection of fluoride in mouthwashes :

Step 1 : Stock solution of $CaCl_2$ in MOPS buffer (1.0 mL) and mouthwash (200 µL) are mixed, and the volume is completed to 2.0 mL with bidistilled water. The concentrations are $[Ca^{2+}]$ = 2.5 mM, and [MOPS] = 50.0 mM, and the mixture contains 10% (v/v) of mouthwash. Solid CaF_2 (10 mg) is added to initiate precipitation, the mixture is vigorously shaken, and left to equilibrate at room temperature for at least 2 hours.

Step 2 : Performed in the same way as in 2.

The obtained fluorescence spectra (λ_{ex} = 316 nm, λ_{em} = 370 nm) are compared to the results shown in Fig. 1 to determine the fluoride content of the solution prepared in *Step 1*, and of the mouthwash sample.

5. Procedure for the detection of fluoride in toothpastes :

Step 1 : 40 mg toothpaste are weighted in a small vial. Stock solution of $CaCl_2$ in MOPS buffer (1.0 mL) and bidistilled water (1.0 mL) are added. The concentrations are $[Ca^{2+}]$ = 2.5 mM, and [MOPS] = 50.0 mM. Solid CaF_2 (10 mg) is added. The mixture is vigorously shaken, sonicated at 50 °C for 15 minutes, and left to equilibrate at room temperature for at least 2 hours.

Step 2 : Performed in the same way as in 2.

The obtained fluorescence spectra (λ_{ex} = 316 nm, λ_{em} = 370 nm) are compared to the results shown in Fig. 1 to determine the fluoride content of the solution prepared in *Step 1*, and of the toothpaste sample.

Note : Toothpastes contain various amounts of water, which were determined as follows : a given quantity of each toothpaste was weighted in a vial, and stored in an oven at 110 °C for 24 hours. By weighting the samples after drying, the water content can be determined :

Sample	% water (w/w)
BHF	37
Elmex Green	55
Elmex for kids	64
Meridol	45
Signal for kids	35

These values imply that the volume of the solution obtained after *Step 1* is not strictly 2.0 mL, but slightly higher. The correction was applied when calculating the concentration of fluoride in the sample.