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A new method for fluoride determination by using fluorophores and dyes anchored onto MCM-41†

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A new colourimetric and fluorimetric method for fluoride determination in aqueous samples based on the specific reaction between fluoride and silica has been developed and applied on real samples.

There has been an increasing interest during the last years in the development and study of new anion chemosensors showing an optical output signal. In the presence of target anions these spectroscopic chemosensors respond by means of a variation on fluorescence (fluoroionophores)[1] or absorbance (chromoionophores),[2] the latter having the advantage of responding to the presence of the target anion with an easily observable colour change. Different approaches have been followed in the design of chemosensors most of them involving the coupling of anion binding sites with chromogenic or fluorogenic signalling subunits. However in most cases colour changes are only observed in non-aqueous solvents such as chloroform or acetonitrile and there are relatively few examples of chemosensors for anion sensing that work in aqueous solution. An alternative method for anion sensing to the anion recognition approach is the use of specific reactions produced by target anions adequately coupled to a signalling event. Following this approach we describe an optical method for fluoride determination in aqueous samples in which we take advantage of the specific attack of fluoride onto silica at acidic pH. The silica is used as support for covalent anchoring of chromophores or fluorophores, then, the presence of fluoride in solution implies the destruction of the silica support and the liberation of the organic molecule to the solution.

Some colourimetric reactions for fluoride determination have been reported involving a recognition approach[3] or displacement reactions[4], for instance the SPADNS colorimetric procedure in which fluoride is reacted with the Zr-SPADNS dye to form the colourless complex $[ZrF_6]^{2-}$.[5] The main inconvenience of these methods is the presence of important interferences as many anions compete with fluoride for the cation coordination and also many cations compete for the fluoride coordination.

The success of our approach is based on the coupling between a silica matrix and a sensing molecule. The former has been chosen from the mesoporous solids of the **MCM-41**[6] family due to its optimal characteristics. Thus, its large surface area (*ca.* 1000 $m^2 g^{-1}$) allows a high degree of functionalization which, in turn, will be translated to a higher response of the final solid. At the same time, the **MCM-41** silica porous system may provide proper protection for the signalling molecules. In addition, the high degree of control previously reached in the synthesis of these materials[7] has allowed us to use an **MCM-41** silica which presents a bimodal pore system. In this way, our inorganic matrix is structured as mesoporous nanoparticles joined together in microsized conglomerates giving rise to a second porous system which is in the range of large-meso to macro in size. This second porous system allows a better accessibility of the target species to the functionalised particles and hence, a quicker response of the solid to the presence of fluoride.[8] The control of the synthesis conditions leads to a system that allows the use of quite mild conditions and the reactions are carried out at room temperature at pH = 2.5 to ensure quantitative formation of HF ($pK_a = 3.20$).

Another important point to ensure the proportionality of the response to the fluoride concentration has been the covalent grafting of the signalling molecule to the silica matrix, because its simple adsorption on the **MCM-41** would result in a discharge of the dye to the solution by leaching instead of by fluorhydric attack. In this sense, special care has been taken in the functionalization process of the matrix. Hence, the synthesis of **S1**, **S2** and **S3**[9] for the colourimetric and fluorimetric measurements has been carried out following the procedure described in Scheme 1. In general, the mesoporous **MCM-41** solid is first functionalised with 3-aminopropyltriethoxysilane in refluxing toluene. Reaction of this amino-functionalised solid with 9-anthraldehyde (in EtOH abs. 45 °C; then with $NaBH_4$ in EtOH, RT), 4-{2-[4-(dimethylamino)phenyl]diazenyl}benzoic acid (DCC–TsOH, 0 °C) and lissamine rhodamine B sulfonyl chloride (in CH_2Cl_2, 0 °C), results in the synthesis of **S1**, **S2** and **S3** respectively. The so obtained solids were exhaustively washed with ethanol in a Soxhlet for 1 or 2 days to remove any excess of reagent or adsorbed indicator, and were characterised with adequate techniques.

Fluoride determination using **S1**, **S2** and **S3** was carried out in acetonitrile : water 7 : 3 (v/v) solutions buffered to pH = 2.5 with 0.1 M potassium hydrogenphthalate and HCl acid. Acetonitrile was used as co-solvent in order to improve the solubility of the organic signalling molecules that are usually lightly soluble in water. In a typical experiment a suspension of the corresponding solid was prepared using 1 mg of solid per 1 mL of buffer. This mixture was then sonicated for 10 min to disperse the particles of the solid and obtain the maximum homogeneity possible in the suspension. Fluoride samples were added to this suspension in polypropylene vials and left stirring for 2 h at room temperature. After this time, the suspensions were filtered and the solutions obtained were directly introduced into the cuvette and measured by the corresponding method, fluorimetric for **S1** and **S3** and colourimetric for **S2** and **S3**. Fig. 1 shows the variation of fluorescence with fluoride concentration when using solid **S1** as the fluoride fluorogenic reagent.

Functionalised solids **S1**, **S2** and **S3** can also be obtained in a monolithic conformation. This allows an easy method to quantify by eye the amount of fluoride in solution. Thus, addition of functionalised monoliths of **S3** to buffered solutions containing fluoride gave, after approximately half an hour, solutions whose colour was proportional to the amount of fluoride. Fig. 2 shows a colour scale obtained upon addition of **S3** solid to fluoride solutions of different concentration.

In order to check the potential applicability of this reaction, we have applied our method to the quantitative determination of fluoride in a commercial toothpaste[10] and a very good

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† Electronic supplementary information (ESI) available: IR spectra, SEM images, X-ray diffraction patterns and TG/TD analysis. See http://www.rsc.org/suppdata/cc/b1/b111128k/

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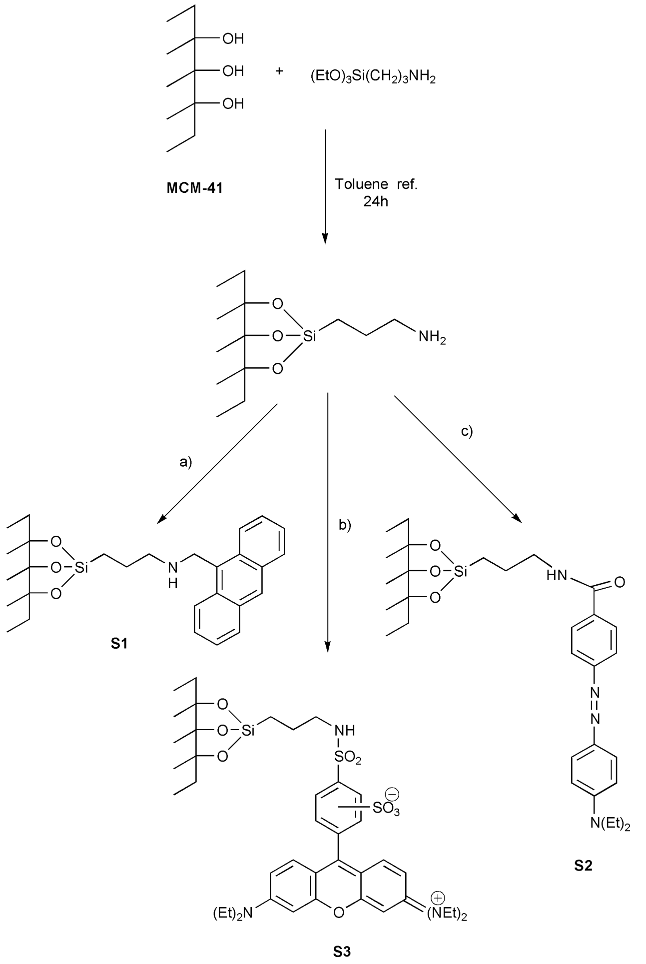

Scheme 1 Synthesis of **S1**, **S2** and **S3** by functionalization of an **MCM-41** matrix firstly with 3-aminopropyltriethoxysilane and then with a) 9-anthraldehyde, b) lissamine rhodamine B sulfonyl chloride and c) 4-{2-[4-(dimethylamino)phenyl]diazenyl}benzoic acid.

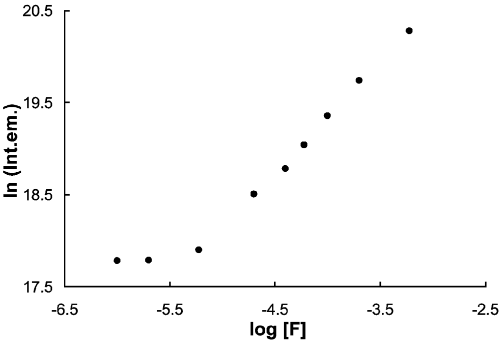

Fig. 1 Evolution of the fluorescence intensity of anthracene in the final solution (after fluoride attack on solid **S1**) *vs.* the concentration of fluoride in the initial solution.

agreement with the claimed concentration has been found (see Table 1). It is noticeable that other colourimetric methods, such as the SPADNS Colourimetric Procedure for the determination of fluoride in toothpaste,[5] present serious deviations (even 67%) in solutions deliberately contaminated with pyrophosphate ($P_2O_7^{4-}$, 0.32%), an anion that is usually present in toothpastes, meanwhile following the approach described here the determination of fluoride on samples containing a ten molar excess of phosphate with respect to fluoride gave errors of less than 8%.

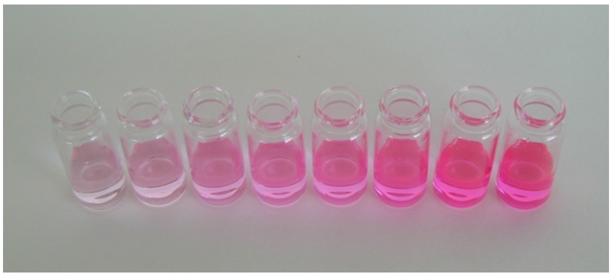

Fig. 2 Colours obtained after reaction of solid **S3** with solutions containing different concentrations of fluoride. From left to right the fluoride concentrations are; 0, 5×10^{-6}, 10^{-5}, 5×10^{-5}, 10^{-4}, 2×10^{-4}, 6×10^{-4} and 2×10^{-3} M.

Table 1 Results of the analysis of a commercial toothpaste based on the reaction of fluoride with functionalised solids **S1**, **S2** and **S3** at pH 2.5.

	S1	S2	S3	Theoretical
% F^- (w/w)	0.25	0.22	0.25	0.24

In summary, we have reported for the first time a new method for determination of fluoride in water based on the specific reaction of fluorhydric acid with a **MCM-41** solid functionalised with fluorescent or colourimetric signalling units. The good results obtained in the determination of fluoride content in toothpaste suggests its potential use as a practical method for the determination of fluoride anions in water samples. The results also point out how the use of specific reactions can be a suitable and alternative method for the development of systems for anion determination.

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10 A toothpaste sample was prepared by suspending 2 g of paste in 30 mL of bidistilled water and stirring for 2 h at 60 °C in a polypropylene vessel and then filtering to eliminate solids in suspension, washing with some water and increasing the volume to 50 mL.