

Reversible Optical Sensor for *In Situ* Determination of Heavy Metal Impurities in the Environment

Renata Reisfeld* and Dimitry Shamrakov

Department of Inorganic Chemistry,
The Hebrew University, Jerusalem, Israel

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The method developed for reversible determination of cadmium ions is based on the incorporation of 8-hydroxyquinoline-5-sulfonic acid into silica films prepared by the sol-gel method. When exposed to a solution containing cadmium ions, a colored complex is formed. The concentration of the colored complex is determined from its characteristic absorption in the visible region using a special apparatus. The detection limit is of sub ppm order. This method can be used for the determination of various heavy metal ions.

1. Introduction

The sensitive detection of pollutants such as heavy metal ions is of particular significance in environmental analysis. For example, divalent cadmium, found in underground water due to careless disposal of cadmium nickel batteries is extremely toxic and its sensitive and reversible detection is required. Here we propose a new method by which a chemical reagent for a metal ion is incorporated into a glass film prepared by the sol-gel method.^(1,2) A colored complex, which is the result of the reaction between the metal ion in the solution and the reagent in the film, can be detected by its optical absorption or fluorescence upon excitation by a light source. The reversibility of the system results from the fact that the bond between the reagent and the glass matrix is stronger than that between the reagent and cadmium. While the reversibility of the system was previously reported for gases such as ammonia,^(3–5) here for the first time a heavy metal ion is shown to be

*Holding a Chair of Solar Energy in the name of Enrique Berman.

reversibly detected. The detection limit is ten ppb. The system can be applied for monitoring and detecting heavy metal ions in remote places.

Reversible and sensitive ion sensors are urgently required for environmental, clinical and industrial applications. A challenging approach is to set the sensors in remote places that cannot be reached easily by conventional sampling. Essential conditions for such an *in situ* sensor to be effective are that the sensing device should be reversible and the signals could be recorded by electrooptic means, such as a fiber optic device. A glass-based sensor is ideal for this application because of its stability and optical transparency which is required for the light wave guiding.

Sensors based on immobilization of reagents on glass prepared by the sol-gel method via the hydrolysis and polycondensation of esters of silicic acid have recently been described.⁽¹⁻¹⁰⁾ However, with the exception of gaseous ammonia and aqueous hydrogen ions no reversibility has yet been obtained. An optical sensor for irreversible determination of Cd(II) was prepared by immobilizing quinoline-8-sulfonate on an ion-exchange resin and attaching the resin to the end of a fiber optic bundle. The detection limit was 10^{-6} M.⁽¹¹⁾

Surface-enhanced Raman spectroscopy (SERS) was applied for determination of Pb(II), Cd(II) and Cu(II) using a 4-(2-pyridylazo) resorcinol (PAR) coating modified with sulfide which allowed attachment to the silver substrate. The detection limit of Cd was reported to be 50 ppb.⁽¹²⁾

An optical fiber fluorosensor for Cd using diethylamino-ethyl Sephadex ion-exchange resin was recently described.⁽¹³⁾ Here we report the first successful attempt to detect reversibly and determine quantitatively a heavy metal ion as exemplified by cadmium in a sensor prepared by the sol-gel method.

2. Experimental

As the reversible reagent for cadmium ions, we used 8-hydroxyquinoline-5-sulfonic acid (abbreviated here as HQ) which forms a strong complex with cadmium in aqueous solution. The excitation and the emission spectra of the complex are shown in Fig. 1. In order to obtain reversibility, which cannot be achieved in aqueous solution, we incorporated the reagent into a glass film deposited on a glass support by the method described in refs. 2 and 3. The glass films were prepared by dip coating in a tetraethoxysilane solution, followed by hydrolysis and polycondensation at room temperature. HQ, which is a weak acid, served as both a reagent for cadmium and a catalyst. Under these specific conditions, films deposited on glass plates having porosity adequate to immobilize the reagent were obtained. A strong bond is formed between the sulfonic group of the reagent (formula of which is presented in Fig. 2), and the silanol groups of the glass. When such a glass plate is placed in a cadmium solution, a labile complex is formed between cadmium and HQ which can be easily decomposed by water flow which removes the cadmium ions, leaving the reagent in the glass film ready for the successive reaction.

We propose the following explanation for such behavior. While the hydroxyls of the sulfonic group are firmly attached to the pores of the glass film, which, in effect leads to binding of the reagent in the glass, the hydroxyl group para to the sulfonic group and

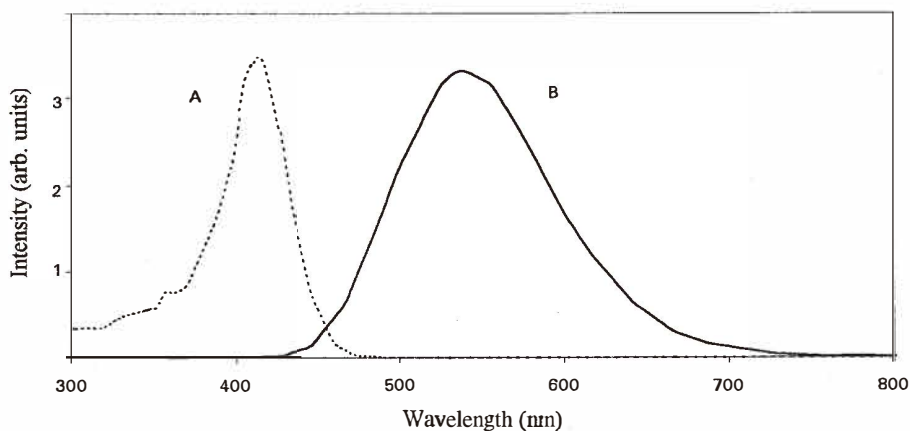


Fig. 1. The excitation (A) and emission (B) spectra of Cd-OxSO₃H₂ complex in water.



Fig. 2. Structural formula of the 8-Hydroxyquinoline-5-sulphonic acid reagent for cadmium ions. The OH group of SO₂OH is attached to the glass film. The OH group adjacent to nitrogen N and the nitrogen atom form a bidentate chelating complex with cadmium.

adjacent to the nitrogen atom which faces the solution forms a labile complex with the cadmium ion. When water flows through, the dynamic equilibrium is responsible for decomposition of the complex, resulting in the free HQ. The experimental setup of a sensor based on the above rationalization is presented in Fig. 3. Eight glass plates covered with HQ-doped glass film are inserted into a transparent cell equipped with inlet and outlet tubes for the alternate flow of the cadmium solution and pure water. The cell was inserted into the Jasco FP770 spectrofluorimeter. The excitation was performed with 390 nm light perpendicular to the active film surface and the emission detected as the luminescent light with a maximum intensity at 530 nm was collected from the edges parallel to the active surfaces. The 390 nm excitation does not correspond to the maximum absorption but allows a better separation of the fluorescence from excitation light. Solutions with decreasing concentrations of cadmium were passed through the compartment, each pass followed by a flow of deionized water at a constant rate of 10 ± 1 ml/min.

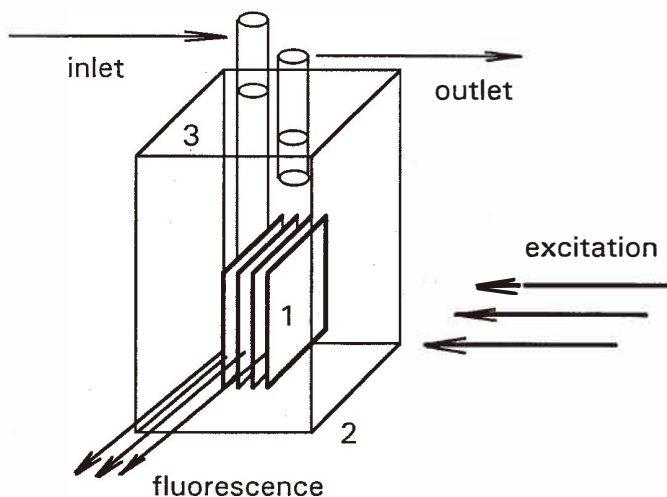


Fig. 3. A scheme of the sensor compartment: 1) glass plates covered with glass film incorporating the reagent. The fluorescence of the complex is concentrated at the plate edges as in the luminescent solar concentrator in ref. 14 for increased sensitivity of detection; 2) transparent cell; 3) container with inlet and outlet glass tubes.

3. Results

The response diagram of fluorescence intensity versus flow time of various solutions is presented in Fig. 4. As can be seen from the figure a complete reversibility of the system has been obtained. The detection limit is 10 ppb of cadmium ions. We believe that an even lower detection limit can be achieved using improved optics such as a small concentrated light source and a light detector connected via fiber optics to the plates.⁽¹⁴⁾

The experiments with the sensor were conducted for two weeks. After the initial signal decrease, no further sensor deterioration was observed. The initial decrease for the very first run can be attributed to the fact that the freshly prepared layer is oversaturated with the reagent which is washed out in the initial stage.

4. Conclusions

Fluorescence analysis is widely used to detect impurities in solutions.⁽¹⁵⁾ The method proposed here can utilize a variety of fluorescent reagents which will be immobilized in the glass light wave guides.

The proposed sensor is not intended to compete with conventional analytical instrumental methods such as atomic absorption spectroscopy or electrochemistry. These methods are obviously much more sensitive. However, all of them require some kind of

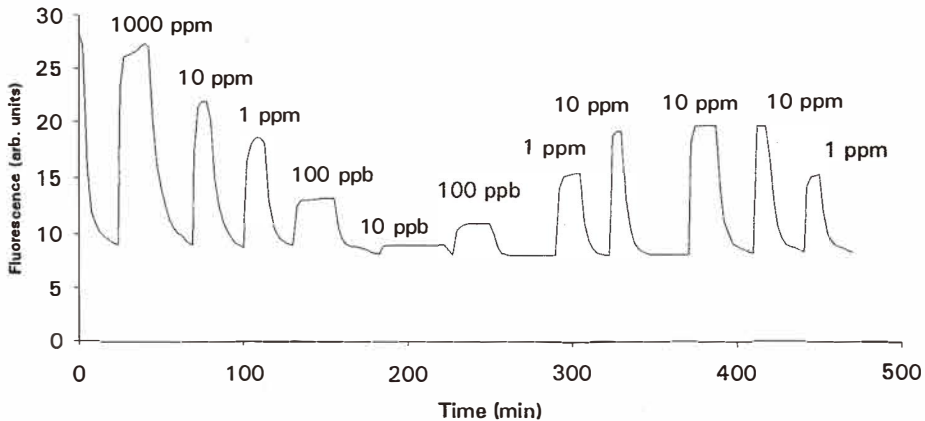


Fig. 4. The fluorescence sensor response to different Cd concentrations in water. The increases in the diagram correspond to the addition of Cd to the flowing solution while the beginning of the decrease corresponds to the initiation of deionized water flow.

sampling and electrode regeneration. In contrast, the reversible optical sensor designed in the fiber optic configuration enables remote automatic monitoring and has an alarm control.

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