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DESIGN NOTE

A compact optical flow cell for use in aqueous halide determination

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Abstract. A compact optical flow cell for use in aqueous halide determination has been developed. The performance of the cell and optical set-up has been tested by studying the halide quenching of fluorescence from thin polymeric films containing a halide-sensitive fluorophore. Aqueous halide is injected into the flow cell and the quenched fluorescence emission observed orthogonal to the plane of excitation after it has undergone total internal reflection within the glass support—an efficient method for observing weak fluorescence intensities. The experimental set-up is both a low-cost and an accurate method for use in the determination of aqueous halide ions. The method can very easily be adopted to determine other aqueous anions which quench the fluorescence of dyes incorporated into thin hydrophilic polymer films. The suitability of this method for the continuous measurement of halide 'on-line' rather than a single 'static' measurement is discussed.

Keywords: flow cell, optical, sensor, halide

1. Introduction

During the past decade much has been published on the development and characterization of luminescence based plastic sensors, especially for the detection of oxygen [1–3], carbon dioxide [4, 5] and ammonia [6, 7]. However, relatively little attention has been paid to thin-film halide sensors [8–10]. This is quite surprising since halide determination is important in many areas of life, including medicine (human plasma [11] and urine [12]), food stuffs (cheeses [13] and wines [14]) and industry (nuclear materials [15], cements [16] and photographic emulsions [17] to name but a few).

The fluorescence quenching of fluorophores by halide was first described by Stokes [18] in 1869, when he observed that the fluorescence intensity of quinine in dilute sulphuric acid was reduced after the addition of hydrochloric acid, i.e. chloride ions. The process that he observed is now commonly referred to as 'dynamic fluorescence quenching' whereby both the lifetime and the intensity of fluorescence are reduced in the presence of a quencher, Q. This process is known to follow Stern–Volmer kinetics [19]

$$I_0/I = 1 + k_q\tau^0[\mathrm{Q}]. \qquad (1)$$

Equation (1) can be used to obtain values of $k_q\tau^0$ (the Stern–Volmer constant, K_{SV}), by plotting I_0/I as a function of [Q], where I_0 and I are the fluorescence intensities in the absence and presence of Q respectively, k_q is a specific constant describing bimolecular collisional deactivation of electronic energy and τ^0 is the natural fluorescence lifetime.

In this design note we present a simple optical flow cell which can be used for the determination of aqueous halide ions. The cell and optical set-up are of low cost, of suitable size for handling and transport, can be used both for static and for on-line measurements and are designed to use sensor films which can be cast on disposable glass microscope slides.

2. Sensor films

The performance of the flow cell was tested using a thin-film sensor for aqueous halide developed by the authors [20], in which a halide-sensitive fluorophore is incorporated into a hydrophilic crosslinked copolymer. The copolymer typically swells by about 200 μm in aqueous media, allowing the diffusion of halide to dynamically quench the fluorescence [19] of the supported dye. The absorption maximum of the dye in the sensor film was 360 nm whilst the fluorescence-emission maximum was Stokes shifted some 100 nm to about 460 nm.

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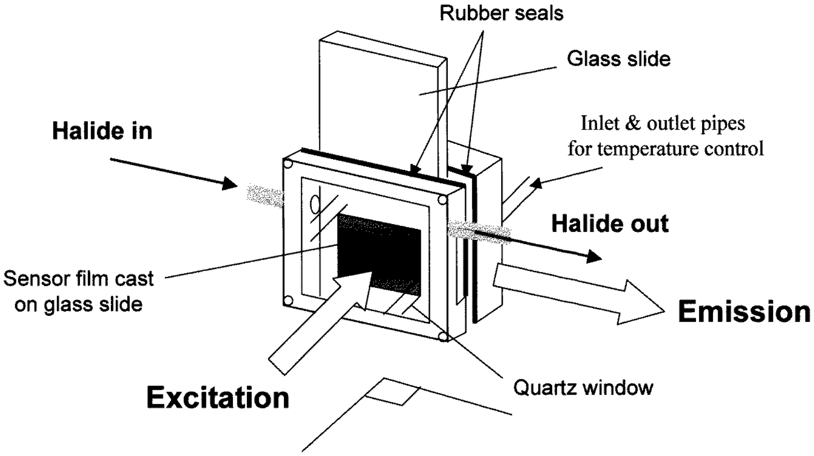

Figure 1. The optical flow cell.

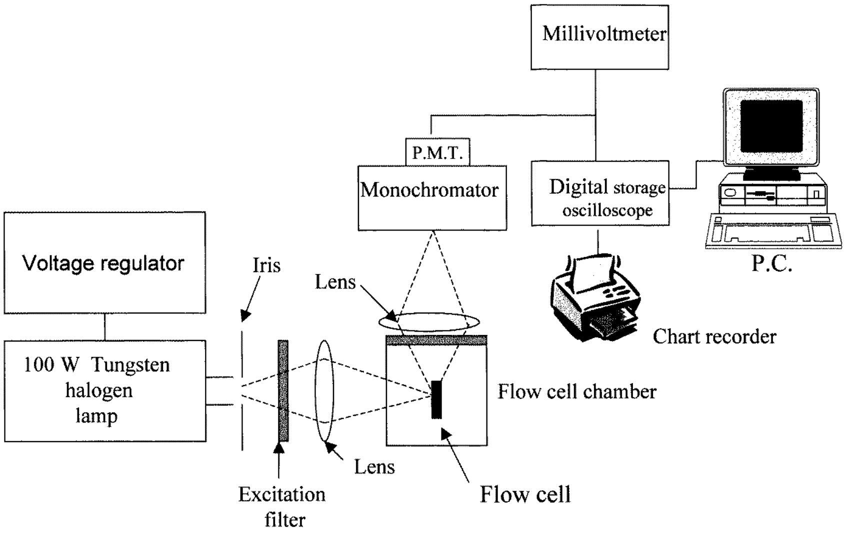

Figure 2. The optical set-up. P.M.T.: photomultiplier tube.

3. The optical flow cell, excitation source and detector

A 1 cm × 1 cm 'cup' with a quartz window and two rubber rings was used to trap a sensor film and give a sealed flow cell, through which aqueous halide solutions were pumped over the sensor film, figure 1. The optical cell is made of brass, with a hollow back and inlet and outlet pipes through which a constant cell temperature is maintained. The cell is blackened to reduce scattering of the excitation light. Light from a 100 W stabilized tungsten halogen lamp is passed through a band-pass filter (typically 320–510 nm transmission in this case, although in practice a monochromator could be used to select the desired wavelength of a different dye) and made incident on the film at 90° to the plane of the slide support. Because of the entrapment of fluorescence emission by total internal reflection within the glass support, the emitted light is conveniently collected from one edge of the slide, passed through a 520 nm cut-off filter and made incident on a Hammamatsu R928 photomultiplier, figure 2. The photomultiplier signal was stored using a Gould OS4020 storage oscilloscope.

4. Data analysis

To maintain an overall constant refractive index upon halide injection, i.e. a constant solution–solution interfacial refraction, a constant solution–film interfacial refraction [21] and a constant ionic strength, all quenching measurements were carried out using solutions containing 1 mol dm^{-3} sodium nitrate. (The sensor films were not quenched by 1 mol dm^{-3} sodium nitrate solution.) The films were firstly blanked with the high-ionic-strength background and the system was calibrated (i.e. the position of zero fluorescence quenching was determined) before the halide solution was injected into the cell.

To determine sensor film Stern–Volmer constants from plots of I_0/I as a function of [Q], equation (1), known concentrations of halide were injected into the flow cell, stepwise (starting from the most dilute halide solution), until sufficient data points had been collected to produce a linear plot. Least squares linear regression analysis of the data was performed using the Axum graphics software package.

For the determination of single halide concentrations, for which the Stern–Volmer constant had been determined

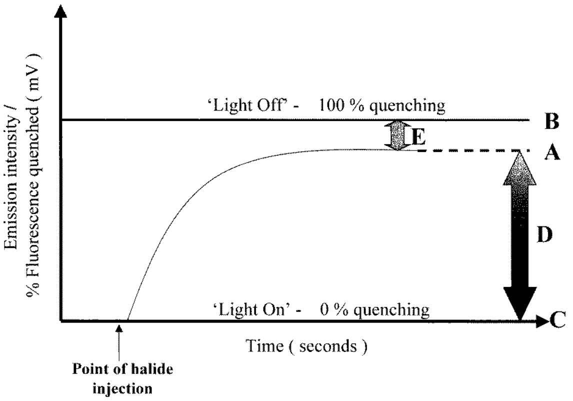

Figure 3. A typical oscilloscope display. The millivoltmeter is used in conjunction with the oscilloscope at high degrees of fluorescence quenching to obtain accurate values. A, The light intensity (mV) in the presence of halide ions; B, 'light off', the position of 100% fluorescence quenching; C, 'light on', the position when no halide is present; D, the quenched emission intensity (mV); and E, the final observed emission intensity (mV).

previously, the halide sample was simply injected into the flow cell, the quenched fluorescence emission intensity noted and the concentration determined from equation (2).

Traces showing photomultiplier voltages as a function of time after halide injection were collected on the oscilloscope. Small changes in the photomultiplier voltage were measured in conjunction with the oscilloscope using a Beckman Industrial DM78 millivoltmeter. Figure 3 shows how the oscilloscope display and millivoltmeter are used together to calculate the halide concentration.

From figure 3 it can be seen that $C - B$ is the relative light intensity of the sensor film in the absence of halide ions and $A - B$ is the relative light intensity of the sensor film in the presence of halide ions. Hence the Stern–Volmer constant can be obtained, from equation (1), by plotting $(C - B)/(A - B)$ against [Q]. Similarly, the concentration of halide [Q] can, if the Stern–Volmer constant is already known, be determined from

$$[\mathrm{Q}] = \frac{1}{K_{\mathrm{SV}}}\left(\frac{C - B}{A - B} - 1\right). \qquad (2)$$

5. The sensor-film size

Various sizes of sensor film were cast onto glass supports to investigate whether the presence of dye molecules in areas of sensor film cast outside the area of the quartz window and hence not directly excited or quenched was important. Although no size effects were observed, all sensor films used in this study were cut slightly smaller than the area of the quartz window, so that all of the sensor film was exposed to the excitation light and all of the sensor film was accessible to the diffusion of aqueous halide ions.

6. The sensor-film response times

Response times for the sensor film to respond to aqueous halide were determined using the instrumentation shown in figures 1 and 2. At the point of halide injection the digital storage oscilloscope was triggered and the response curve observed. Figure 4 shows a typical response curve of a sensor film quenched by molar halide solutions at 20 °C. The times for 90% of the response to molar halide were 30–60 s whereas the times for 90% of the response to more dilute halide solutions were much longer. The reversibility of the system was demonstrated by washing the film with distilled water, the fluorescence of the dye returning as the halide is removed. To return the film fluorescence to its original unquenched intensity required washing with 1 mol dm^{-3} nitrate solution for approximately 180 s. (The volume of nitrate typically used was approximately ten times that of halide).

It is interesting to note that, at the point of halide injection into the flow cell, figure 4, point a, there is a period of about 2–5 s during which no fluorescence change is observed. This is thought to be primarily due to the filling of the flow

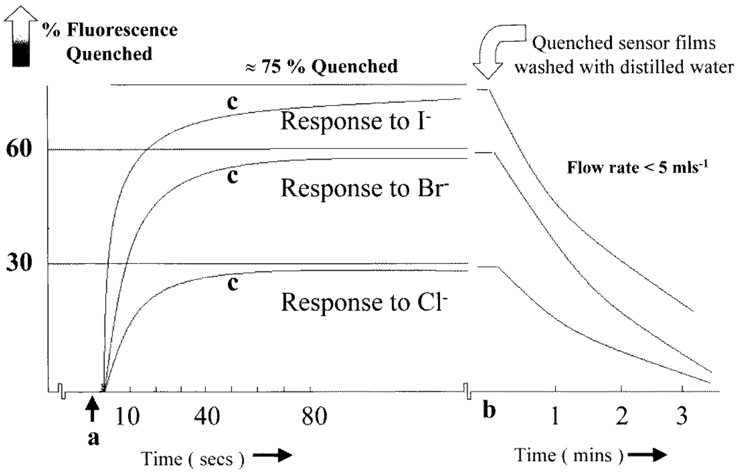

Figure 4. The sensor-film response to 1 M halide solutions. The same film is used for all three response curves. Washing quenched films with distilled water returns the films to their original fluorescence intensity. a, The point of halide injection at time $t = 0$; b, the point of injection of distilled water into the flow cell; and c, the roughly 90% sensor-response point.

cell with aqueous halide rather than actual diffusion of halide within the sensor film, since the pre-swollen sensor film is very thin (≈250 μm, measured using a Digi-Cal dead-weight micrometer). Although the response time is not particularly important for large-volume measurements, such as the continuous on-line quality control of halide in water supplies or photographic solutions, static measurements in smaller volumes may require a flow cell of smaller volume with inlet pipes with a greater internal diameter; in either case, miniaturization is likely to increase the cost. Increasing the rate of halide flow into the cell to values greater than about 5 ml s^{-1} tended to cause the solution to breach the rubber seals. Approximately 30 cm^3 of sample is needed for a measurement, the sample 'cup' having a volume of about 10 cm^3.

7. Conclusions

The conclusions resulting from this study can be summarized as follows.

(i) An optical flow cell for use in the determination of aqueous halide ions has been developed.
(ii) The instrumentation required for halide analysis by this method is of low cost and is of a practical size both for laboratory and for industrial use.
(iii) The cell is designed to use sensor films which are cast on disposable glass slides.
(iv) Collecting fluorescence emission by this method is very efficient, an important consideration when measuring low fluorescence intensities, i.e. at high degrees of fluorescence quenching.
(v) The method can be used both for continuous halide monitoring and for single halide measurements; the minimum sample volume required for a single measurement is about 30 ml.
(vi) The optical flow cell can be used in the determination of other aqueous ions when the dyes sensitive to the ions in question are also incorporated 'into' or 'onto' a plastic or glass support.

Acknowledgments

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References

[1] Demas J N and DeGraff B A 1995 *J. Anal. Chem.* **67** 1377
[2] Demas J N and DeGraff B A 1993 *J. Anal. Chem.* **65** 3480
[3] Demas J N and DeGraff B A 1991 *J. Anal. Chem.* **63** 332
[4] McMurray H N 1992 *J. Mater. Chem.* **2** 401
[5] Mills A and Monaf L 1996 *Analyst* **121** 535
[6] Wolfbeis O and Posch H 1986 *J. Anal. Chim. Acta* **185** 321
[7] Mills A, Chang Q and Wild L 1995 *Mikrochim. Acta* **121** 225
[8] Wolfbeis O, Offenbacher H and Urbano E 1984 *J. Anal. Chem.* **56** 427
[9] Bright F, Zhu C and Hieftje G 1990 *Appl. Spectrosc.* **44** 59
[10] Habib Jiwan J-L and Soumillion J-Ph 1997 *J. Non-Cryst. Solids* **220** 316
[11] Osterloh H O 1984 *J. Vet. Human Toxicol.* **26** 412
[12] Vallon J J and Pegon Y 1980 *J. Anal. Chim Acta* **20** 65
[13] Portviet I J and Horwitz W 1982 *J. Assoc. Offic. Anal. Chem.* **65** 1350
[14] Verma K K 1987 *J. Food. Chem.* **25** 269
[15] Overman R F 1971 *J. Anal. Chem.* **43** 616
[16] Yamada A 1990 *J. Bunseki Kagaku* **39** 295
[17] James T H 1977 *The Theory of the Photographic Process* 4th edn (New York: MacMillan)
[18] Stokes G G 1869 *J. Chem. Soc.* **22** 174
[19] Stern O and Volmer M 1919 *M. Phys. Z.* **20** 183
[20] Geddes C D 1996 Optical thin film sensors for the determination of aqueous halide ions *PhD Thesis* University of Wales, Swansea
[21] Demas J N and Crosby G A 1971 *J. Phys. Chem.* **75** 991