

Optical Thin-Film Sensors for the Determination of Aqueous Halide Ions

Chris D. Geddes,^{1,3} Peter Douglas,¹ Christopher P. Moore,² Trevor J. Wear,² and Peter L. Egerton²

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Fourteen thin-film optical sensors in which halide-sensitive fluorophores are immobilized in a thin copolymer film ($\approx 50 \mu\text{m}$, dry) have been developed and characterized. The sensor films use rhodamine, 6-methoxyquinoline, and harmane dyes which have been functionalized and bound to a hydrophilic copolymer. The sensor films are reversibly capable of determining aqueous bromide and iodide with ≈ 4 and 2% accuracy, respectively, at concentrations of around $10^{-3} \text{ mol dm}^{-3}$, and are more sensitive than previous plastic sensor fabrications. The 90% response time to molar iodide is $\approx 30\text{--}60 \text{ s}$. A combination of sensor films allows the simultaneous determination of both I^- and Br^- in a mixed-halide solution. The interference of several ions, including *pseudo*-halides, on the sensor films has been studied.

KEY WORDS: Thin film; sensor; halide; fluorescence quenching.

INTRODUCTION

Halide determination is important in many areas of everyday life, including *foodstuffs*—wines [1], fruit juices [2], and cheeses [3]; *industry*—nuclear materials [4], cements [5], petroleum/crude oils [6], explosives [7], and photographic materials [8]; and *medicine*—where the determination of halide in blood [9], serum [10], plasma [11], and urine [12] is of obvious importance.

Over the past 10 years there has been extensive literature published on the development and characterization of luminescent-based plastic sensors, especially for the detection of oxygen [13–16], carbon dioxide [17,18],

and ammonia [19,20]. However, little attention has been paid to thin-film halide sensors [21,24].

Fluorescence quenching of immobilized dyes as a method of halide detection was first utilized by Wolfbeis *et al.* [21]. In a series of papers Wolfbeis and co-workers synthesized a group of highly fluorescent dyes and demonstrated the simultaneous detection of mixed halides using the extended Stern–Volmer equation [22,23]. Immobilization of these dyes to the surface of a glass substrate produced a sensor device for the individual detection of either chloride, bromide, or iodide in aqueous solutions [23] which was capable of detecting iodide or bromide with ≈ 3 and 4% accuracy at concentrations around $10^{-3} \text{ mol dm}^{-3}$. In addition to this work, Bright *et al.* have used quinine and harmane derivatives immobilized in cellulose, on a fiberoptic device, for the simultaneous determination of aqueous bromide and iodide [24]. Their sensor performance was such that $0.004 \text{ mol dm}^{-3}$ Br^- and I^- could be detected with $\approx 5\%$ accuracy.

In this paper 14 new halide sensor films are characterized. The sensor films have been produced by binding

¹ Department of Chemistry, The University of Wales Swansea, Singleton Park, Swansea, South Wales SA2 8PP, UK.

² Kodak Ltd., Headstone Drive, Harrow, Middlesex HA1 4TY, UK.

³ To whom correspondence should be addressed at Department of Physics and Applied Physics, The University of Strathclyde, John Anderson Building, 107 Rottenrow, Glasgow G4 0NG, UK. e-mail: c.d.geddes@strath.ac.uk

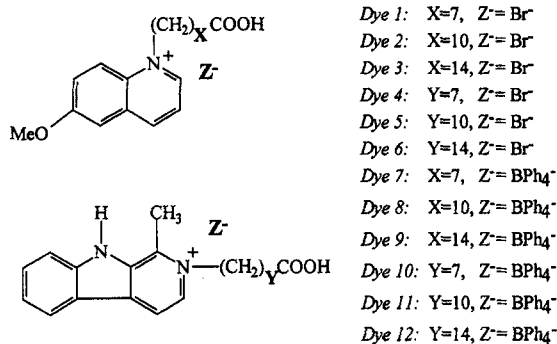


Fig. 1. Dyes 1–12.

highly fluorescent water-soluble dyes (Fig. 1) to a hydrophilic copolymer [25] (Fig. 3). The copolymer typically swells by $\approx 200 \mu\text{m}$ in aqueous media. The fluorescence of the sensor films is dynamically quenched by aqueous halide ions between pH 7 and pH 11. Combinations of dye sensor films used to determine single and multiple halide concentrations employ both the Stern–Volmer equation and extended Stern–Volmer equations, both reviewed many times [23,26]. The reasons for choosing the dyes employed here are that they are water soluble, soluble in the polymer, and sensitive to aqueous halide over technological and medically important pH ranges, have different Stern–Volmer quenching constants for aqueous chloride, bromide, and iodide ions [23], and are suitable for covalent attachment to the copolymer. The sensor films are completely reversible, cheap, and disposable and allow a more accurate determination of halide as compared to previous plastic sensor fabrications [24]. Response to halide is compared for dyes in solution and dyes unbound and bound in copolymer films. (Unbound dye refers to dye mixed in the copolymer solution before casting and cross-linking, compared to bound dye, where dye is covalently attached to copolymer.) Our particular interest in these sensors lies in their potential use in photographic processing equipment, which often operates with mildly alkaline solutions, and we have therefore made most of our studies using a solution pH of 10.

EXPERIMENTAL

Materials

The synthesis of dyes 1–12 has been described previously [25]. Dye synthesis gives bromide salts (dyes 1–6) and counterion exchange was carried out to remove the bromide counterions, which otherwise may act as quenchers themselves. The counterion, BPh₄⁻, was chosen

as an organophilic counterion (dyes 7–12) in the hope that counterion exchange would also improve polymer–dye compatibility [16–18]. All reagents were purchased from the Aldrich Chemical Company and used as received.

Instrumentation and Data Analysis

All steady-state emission and excitation spectra for dye solutions and sensor films were recorded on a Jobin–Yvon JY3D spectrofluorimeter. All excitation spectra are corrected with respect to the xenon arc lamp profile. Steady-state Stern–Volmer analysis of dye solutions 1–12 was carried out at 21°C, pH 10 (Borax Buffer), using halide concentrations in the range $1\text{--}10^{-4} \text{ mol dm}^{-3}$. Subsequently, the Stern–Volmer quenching constants for dyes 1–12 with aqueous halide ions were calculated using the Axum Graphics linear regression program. While Stern–Volmer analysis for dye solutions was carried out on the above spectrofluorimeter, analysis of sensor films was carried out using the following instrumentation [25,27].

A $1 \times 1\text{-cm}$ “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 (Fig. 2). 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 was passed through a suitable band-pass filter [dependent on the dye(s) used] and made incident on the film at 90° to the plane of the slide support. Because of entrapment of fluorescence emission by total internal reflection within the glass support, the emitted light was conveniently collected from one edge of the slide, passed through a suitable cutoff filter, and made incident on an Hamamatsu R928 photomultiplier. The photomultiplier signal was stored using a Gould OS4020 storage oscilloscope. For each dye studied a combination of a band-pass filter on the excitation side and a cutoff filter on the emission side was chosen to allow adequate excitation intensity while preventing light from the excitation beam reaching the detector. We have found that this simple optical arrangement gives a high emission collection efficiency and a low background signal [27].

To maintain an overall constant refractive index upon halide injection, i.e., a constant solution–solution, a constant solution–film interfacial refraction [27,28], 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.)

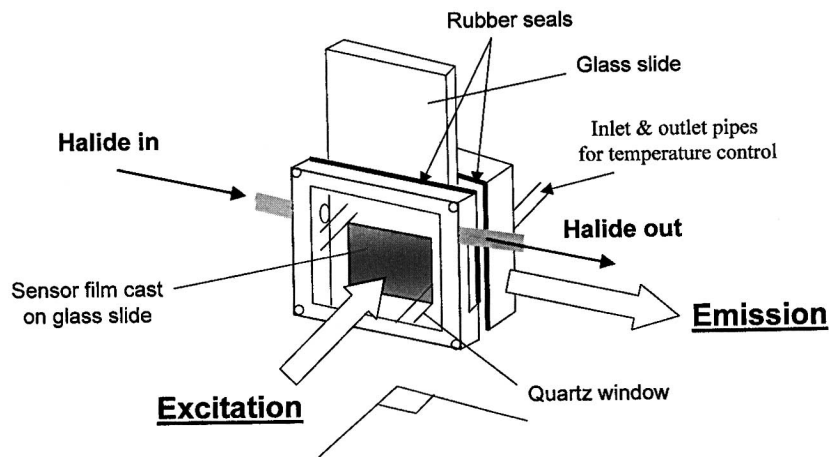


Fig. 2. Flow cell used to mount sensor films.

The films were first blanked with the high-ionic strength background and the system was calibrated (i.e., the position of zero fluorescence quenching determined) before the halide solution was injected into the cell.

To determine sensor film Stern–Volmer constants (K_{SV}), from plots of I_0/I as a function of $[Q]$ (where I_0 and I are the fluorescence intensities in the absence and presence of the quencher Q , respectively), 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 and multiple halide concentrations, where the Stern–Volmer constant(s) had been determined previously, the halide sample was simply injected into the flow cell, the quenched fluorescence emission intensity noted, and the concentration(s) calculated from the Stern–Volmer equation(s).

Bound Dye and Unbound Dye Sensor Films

The attachment of dyes 1–12 to the hydrophilic copolymer, Quattro [29] (Fig. 3), has been described in detail previously [25]. Figure 3 shows the typical linkage of dye 1 to the Quattro copolymer via the hydroxyl group of the Hema (2-hydroxyethyl methacrylate) comonomer unit. Elemental analysis and $^1\text{H-NMR}$ measurements indicate that the bound dye polymer ratio was $<1\%$ (w/w). Dye attachment tended to slightly increase polymer cross-linking. Unbound dye sensor films were prepared by mixing dye with polymer and polymer cross-linking agent as described below.

Sensor Film Formulations

Un-cross-linked polymer (or dyed polymer for bound dye films), 0.5 g, was dissolved in 2.5 ml of ethanol by stirring for ≈ 2 h at room temperature. For unbound dye films this was followed by the addition of 0.01 g of dye and a further 2 h of stirring. For both bound and unbound dye films cross-linking was carried out by the addition of 0.125 g of a polymer cross-linking agent, tripropylamine (TPA), which was added dropwise with rapid stirring. Films were then rapidly cast onto glass slides and cured in a Gallenkamp BS2 fan-assisted oven at 88°C . After curing, films were washed in distilled water to remove excess cross-linking agent. To minimize dye–dye energy transfer, film optical densities were kept very low, ≤ 0.01 . TPA did not quench the fluorescence of dyes 1–12 or the rhodamine dyes.

Sensor Film Casting

Films were cast by sliding a drop of copolymer mixture between two glass slides. After film curing, excess film was cut away. Film thicknesses, determined by a Digi-Cal deadweight micrometer, were reproducible, typically $50\ \mu\text{m}$ dry and $\approx 250\ \mu\text{m}$ wet.

Different areas of sensor film were cast onto glass supports to investigate whether dye–dye energy transfer to areas of sensor film outside the area of the quartz window, and hence inaccessible by halide ions, could contribute to the observed sensor film background fluorescence. Although no effects were observed, sensor films used for halide analysis were still cut slightly smaller than the area of the quartz window. Dye–dye energy transfer is unlikely, as dyes 1–12 typically show $\approx 100\%$

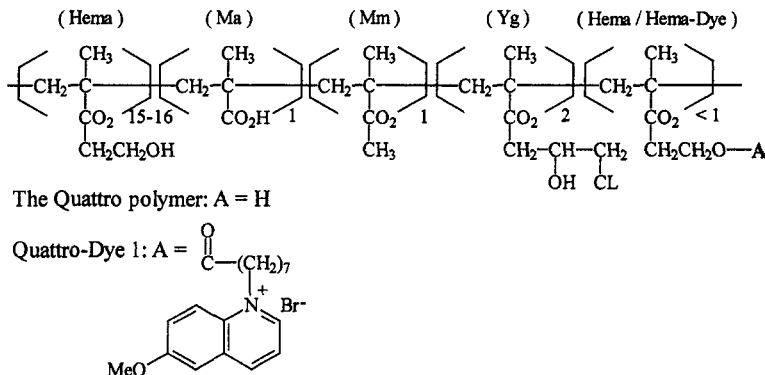


Fig. 3. The Quattro copolymer [poly(2-hydroxyethyl methacrylate)₁₆-co-(methyl methacrylate)₁-co-(methacrylic acid)₁-co-(3-chloro-2-hydroxypropyl methacrylate)₂]; ratios, **16:1:1:2**. Dye 1 bound to the Quattro copolymer [poly(2-hydroxyethyl methacrylate)₁₅₋₁₆-co-(methyl methacrylate)₁-co-(methacrylic acid)₁-co-(3-chloro-2-hydroxypropyl methacrylate)₂-co-(2-hydroxyethyl methacrylate-*dye 1*)_{<1}]; ratios, **15-16:1:1:2: < 1**.

nm Stokes-shifted fluorescence maxima and films were prepared with low, ≤ 0.01 , optical densities. To avoid problems of sensor-to-sensor reproducibility, the same individual sensors were used in both the determination of Stern–Volmer constants (Table II) and the mixed-halide analysis (Table III).

Sensor Film Response Times

Sensor film response times were determined using the instrumentation described earlier. At the point of halide injection the digital storage oscilloscope was triggered and the response curve observed.

RESULTS AND DISCUSSION

The excitation and emission wavelength maxima for rhodamine dyes and dyes 1–12, in solution, unbound and bound to polymer is shown in Table I. The excitation and emission spectra for the unbound and bound dyes are the same as in solution, indicating little or no electronic interaction between the copolymer support and the fluorescent dye molecules. Since the separation between the spectral emission peaks of the 6-methoxyquinoline- and harmane-based fluorophores was not great enough, combinations of dyes in one sensor film could not be achieved. Instead, individual sensor films containing only one dye were used for the determination of halide in single- and mixed-halide solutions.

All solution Stern–Volmer plots are linear, with good linear regression correlation coefficients. However, Stern–Volmer plots for both unbound and bound dye films show negative deviations under conditions of very

efficient quenching, e.g., at iodide concentrations higher than $\approx 0.1 \text{ mol dm}^{-3}$. Even so, for halide concentrations in the range of medicinal and technological interest, i.e., $< 0.1 \text{ mol dm}^{-3}$, both bound and unbound dye sensor films give Stern–Volmer plots of good linearity (Fig. 4). It is generally observed that quenching-based luminescent sensors which are supported in organic or inorganic polymers exhibit nonlinear Stern–Volmer quenching behavior. Two common explanations of the nonlinearity [13–16] are either *multisite dye binding* or the *nonlinear solubility properties* of the dye in the support. The halide concentration at which Stern–Volmer plots deviate from linearity varied from dye to dye and is not discussed further here.

Individual Halide Solutions

The Stern–Volmer constants, K_{SV} , increase for all dyes in solution on going from chloride to bromide to iodide (Table II). For dyes 1–3 and dyes 7–9, there is a general decrease in halide sensitivity as the alkyl chain length, x , increases from 7 to 14. Stern–Volmer constants for BPh_4^- salts are significantly smaller than those for Br^- salts, showing that the counterion has an effect on sensitivity. This may be simply a size effect, the larger counterion sterically hindering halide diffusion to the dye. Alternatively, in sensor films, the organosoluble BPh_4^- ion may solubilize the dye in more hydrophobic regions of the polymer, inaccessible to aqueous halide. This effect is also observed for the harmane dyes, dyes 4–6 and 10–12, respectively. However, the harmane dyes do not show any effect of chain length on Stern–Volmer constants.

Table I. Excitation (λ_{ex}) and Emission (λ_{em}) Wavelength Maxima for the Rhodamine Dyes and Dyes 1–12 in Solution (pH 10, Borax Buffer), Unbound and Bound to Copolymer (Wet Films–H₂O, pH 10)^a

Dye	Solution		Dye solubility in water	Unbound dye sensor films		Bound dye sensor films	
	λ_{ex} (nm)	λ_{em} (nm)		λ_{ex} (nm)	λ_{em} (nm)	λ_{ex} (nm)	λ_{em} (nm)
1	360	460	Very good	360	460	360	460
2	360	460	Very good	360	460	362	460
3	360	460	Very good	360	460	360	460
4	390	460	Good	390	470	390	470
5	390	460	Good	390	470	390	470
6	390	460	Good	390	470	390	470
7	360	460	Good	360	460	360	460
8	360	460	Good	360	460	360	460
9	360	460	Good	360	460	360	460
10	390	460	Fair	390	470	390	470
11	390	460	Fair	390	470	390	470
12	390	460	Fair	390	470	390	470
Rhodamine B	550	580	Very good	550	590	550	590
Rhodamine 6G	530	550	Very good	530	560	—	—

^a Rhodamine 6G was not bound to copolymer.

The Stern–Volmer constants for sensor films are much lower than those for the corresponding dyes in solution. This is probably due to a lower halide diffusion rate in the polymer films. Similarly, the Stern–Volmer constants are significantly smaller in bound as compared to unbound films. This is thought to be due to the increased cross-linking of the polymer during the dye attachment process, which leads to a lower rate of halide diffusion, thus quenching rates in the bound dye films are lower.

The errors in halide determination for individual halide solutions at concentrations around 0.001 mol dm⁻³ for unbound and bound dye 1 films are 2 and 3% for I⁻ and 4 and 6% for Br⁻, respectively. The bound films are less sensitive than unbound films. In comparison, the errors in halide determinations for bound films at concentrations around 0.01 mol dm⁻³ are 1.5 and 2% for I⁻ and 3 and 4% for Br⁻, respectively. The error in chloride detection at 0.01 mol dm⁻³ was found to be ≈7% for unbound films.

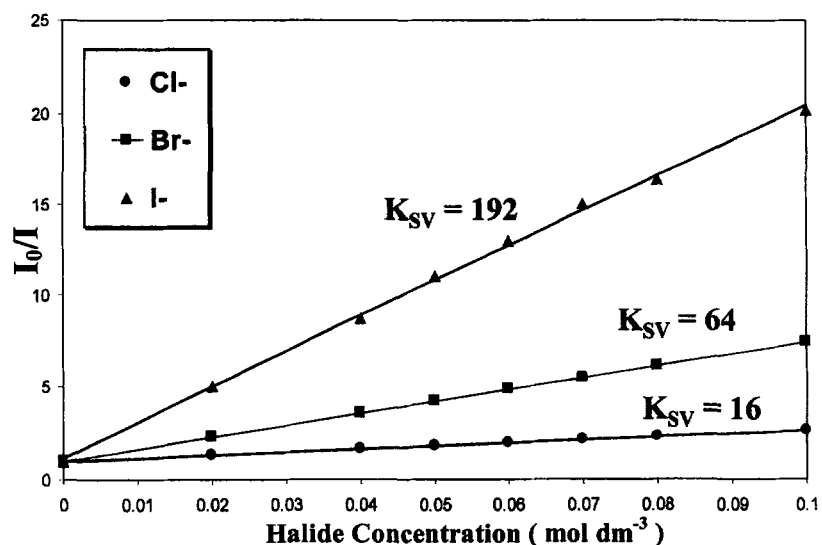


Fig. 4. Stern–Volmer plots for unbound dye 1 sensor films, quenched by aqueous halide ions at 21°C, pH 10. The plots are linear at halide concentrations lower than 0.1 mol dm⁻³.

Table II. Stern–Volmer Constants for Dyes in Solution (Either H₂O, pH 10, or a 50:50, v/v, Mixture of Ethanol and Buffered Water) and in Unbound and Bound Dye Sensor Films^a

Dye	Condition for solution studies	Solution			Steady-state Stern–Volmer constant (mol ⁻¹ dm ³) Unbound films			Bound films		
		Cl ⁻	Br ⁻	I ⁻	Cl ⁻	Br ⁻	I ⁻	Cl ⁻	Br ⁻	I ⁻
1	H ₂ O, pH 10	52	225	634	16	64	192	—	11	66
2	H ₂ O, pH 10	34	150	480	3	14	53	—	—	—
3	H ₂ O, pH 10	34	127	398	4	14	28	—	—	—
4	H ₂ O, pH 10	—	3	191	—	2	15	—	2	7
5	H ₂ O, pH 10	—	5	198	—	2	15	—	—	—
6	H ₂ O, pH 10	—	3	192	—	2	14	—	—	—
7	Ethanol/H ₂ O, pH 10	20	70	218	—	10	47	—	5	29
8	Ethanol/H ₂ O, pH 10	14	55	165	—	11	22	—	4	19
9	Ethanol/H ₂ O, pH 10	11	27	139	—	6	3	—	1	8
10	Ethanol/H ₂ O, pH 10	—	1	139	—	—	8	—	—	1
11	Ethanol/H ₂ O, pH 10	—	1	143	—	—	10	—	—	1
12	Ethanol/H ₂ O, pH 10	—	1	141	—	—	7	—	—	1
Rhodamine 6G	H ₂ O, pH 10	—	—	24	—	—	4	—	—	—
Rhodamine B	H ₂ O, pH 10	—	—	5	—	—	1	—	—	1

^a For all film studies, films were exposed to aqueous halide at pH 10. — indicates no detectable quenching.

Rhodamine B and rhodamine 6G unbound and bound films show errors in iodide determination at 0.01 mol dm⁻³ of ≈2 and 3%, respectively. (Rhodamine 6G was not bound to copolymer and rhodamine B produces similar results for both unbound and bound films.)

The errors for individual halide determination at concentrations around 0.01 mol dm⁻³ for dye 4 unbound and bound films are 2 and 4% for I⁻ and 2 and 2.5% for Br⁻. In comparison, at 0.1 mol dm⁻³ the errors are 1 and 3% for I⁻ and 2% for Br⁻.

Although all studies reported here are for aqueous solutions at pH 10, the sensors are also effective in the pH range 7–11, however, there are some small changes in Stern–Volmer constants over this pH range.

Mixed-Halide Solutions

Analysis of mixed-halide solutions (Table III) with unbound and bound dye sensor films shows results very similar to those obtained for individual halide solutions.

When moderate halide quenching concentrations are used, 0.1–0.05 mol dm⁻³, the typical error in halide analysis is only a few percent. However, for the same dye solutions and films but using higher halide concentrations of 0.5 and 0.3 mol dm⁻³ aqueous I⁻ and Br⁻, the errors in halide analysis are generally much higher, even though the Stern–Volmer constants can be accurately and reproducibly determined in the nonlinear portion of the Stern–Volmer plot. The difference in accuracy at these two

concentration ranges is attributed to the inaccurate measurement of low light intensities at high degrees of fluorescence quenching.

Clearly the level of accuracy in halide determination depends on the halide concentration range being studied and the choice of sensor films employed. In this study low halide concentrations are best determined by dyes or combinations of dyes with large Stern–Volmer constants, while higher halide concentrations require dyes or combinations of dyes with smaller Stern–Volmer constants.

Sensor Film Response Times

The 90% response times (the time for a 90% change in the respective fluorescence signal) of unbound dye films to molar halide are found to lie in the range 30–70 s. The results show slightly longer response times for bound compared to unbound films (Table IV); again, this is thought to be due to the increased cross-linking of the polymer during the dye attachment process. To return the films to their original unquenched intensity required approximately 10 times the volume of water than halide solution, washed over the films at a high flow rate for ≈180 s. Figure 5 shows a typical response for a dye 1 unbound sensor film to molar halide solutions. The reversibility of the film is demonstrated by washing the film with distilled water, the dye fluorescence returning as the halide is removed.

Table III. Some Typical Iodide and Bromide Determinations Using Different Combinations of Two Sensor Films and Two Mixed-Halide Solutions

	Concentration of quenchers (mol dm ⁻³)		Determined halide concentration		% error	
	[I ⁻]	[Br ⁻]	[I ⁻]	[Br ⁻]	[I ⁻]	[Br ⁻]
Solution dye mixtures						
Dye 1/rhodamine B	0.100	0.050	0.100	0.049	0.4	2.0
Dye 1/rhodamine B	0.500	0.300	0.499	0.264	0.2	12.7
Dye 4/rhodamine 6G	0.100	0.050	0.100	0.048	0	4.0
Dye 4/rhodamine 6G	0.500	0.300	0.500	0.366	0.1	22.1
Two single unbound dye films to determine mixed-halide concentrations						
Dye 1/rhodamine B	0.050	0.030	0.050	0.033	0	9.1
Dye 4/rhodamine B	0.050	0.030	0.049	0.031	2.0	3.2
Two single bound dye films to determine mixed-halide concentrations						
Dye 1/rhodamine B	0.050	0.030	0.049	0.033	2.1	9.1
Dye 4/rhodamine B	0.050	0.030	0.052	0.032	3.6	6.6

It is interesting to note that no sensor film showed its fluorescence to be 100% quenched even when very thin sensor films and high halide concentrations were used. This “background fluorescence” could be due to dye buried in the polymer, which is not accessible to halide ions, and this may also account for the negative deviation of Stern–Volmer plots at high halide concentrations.

Dye Leaching from Sensor Films

A typical problem associated with polymeric-based dye sensors, when a sensor film is immersed in solution,

is fluorophore leaching. Unbound dye sensor films soaked in molar nitrate solution, in excess of 2 h at 20°C, typically showed a change of only a few percent in the observed fluorescence intensity. However, bound dye sensor films showed no change in fluorescence intensity, even after very long times.

Sensor Film Selectivity

To ascertain sensor film selectivity, interferences were studied using 0.5 mol dm⁻³ standard solutions of various anions. Sulfite and the *pseudo*-halide, isothiocyanate, were shown to be effective fluorescence quenchers

Table IV. Sensor Film (90%) Response Times to Molar Halide Solutions

Dye in sensor film	Response times to 1 mol dm ⁻³ unbound (90%)			Response times to 1 mol dm ⁻³ bound (90%)		
	Cl ⁻	Br ⁻	I ⁻	Cl ⁻	Br ⁻	I ⁻
1	50	50	50	— ^a	55	50
2	50	50	50	—	—	—
3	50	50	50	—	—	—
4	—	65	65	—	70	70
5	—	70	—	—	—	—
6	—	60	—	—	—	—
7	—	50	50	—	50	40
8	—	50	50	—	60	50
9	—	50	50	—	50	45
10	—	—	60	—	—	60
11	—	—	60	—	—	—
12	—	—	60	—	—	—
Rhodamine B	—	—	35	—	—	40
Rhodamine 6G	—	—	30	—	—	—

^a No response obtained.

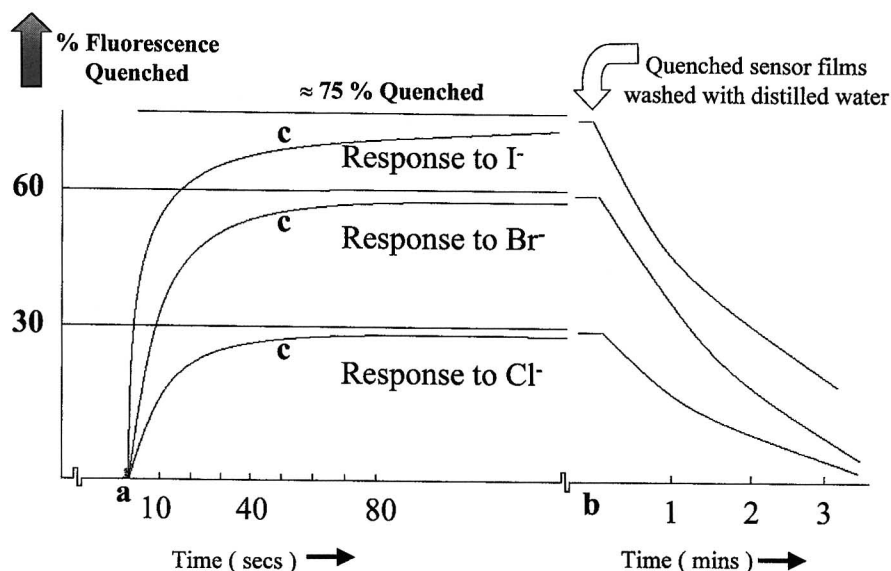


Fig. 5. Unbound dye 1 sensor film response to molar halide solutions. The same film is used for all three response curves. Washing quenched films with distilled water returns the films to their original fluorescence intensity. **a** indicates the point of halide injection at time $t = 0$. **b** indicates the point of distilled water injection into the flow cell. **c** indicates the $\approx 90\%$ sensor response point.

with large Stern–Volmer constants. While one would not normally expect to find these ions in serum and urine, other *pseudo*-halides, such as the anesthetic Halothane, may be present and therefore determinable by a combination of these sensors. No interferences were observed with nitrate, sulfate, and phosphate ions. Interferences can be taken into account by using the extended Stern–Volmer equation, where two sensor films have different Stern–Volmer constants for the interference.

CONCLUSIONS

The thin-film sensors described here can be used for the determination of halides in mixed-aqueous halide solutions at a mildly alkaline pH (pH 10). The determination of n quenchers can be achieved by the use of n sensor films in which a single dye is immobilized.

The sensor films have shown the accuracy of the determination of iodide and bromide at concentrations around $0.001 \text{ mol dm}^{-3}$ to be ± 2 and $\pm 4\%$, respectively. This increased sensitivity over that reported by others is attributed to the larger Stern–Volmer constants of dyes 1–12. The sensor films are completely reversible, with typical response times of 30–70 s, and have a shelf life in excess of 2 years.

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