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Selective Detection of Hydrogen Peroxide Vapours Using Azo Dyes

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A rapid and selective visual colour method is described for detection of hydrogen peroxide (H_2O_2) and peroxide based explosive (PBE) vapours by the combination of three azo dyes – Calmagite, Orange G and Orange II. The bleaching of these dyes by H_2O_2 is catalysed by Mn^{II}. At pH 8.0 (EPPS, N-2-hydroxyethyl-piperazine-N'-3-propanesulfonic acid) Calmagite is quickly degraded but under these conditions Orange G and Orange II are not perceptibly bleached, especially in the presence of ethylenediaminetetraacetic acid (H_4edta). However, fast bleaching of Orange G and Orange II was observed at pH 9.0 (Na_2CO_3, sodium carbonate) due to the in situ formation of the carbonate radical ($CO_3^{-\bullet}$). Hence by a combination of Calmagite at pH 8.0, and Orange G and Orange II at pH 9.0, selectivity to H_2O_2 vapours against Cl_2, NO_2 and O_3 can be demonstrated. Initial studies were carried out on filter papers but reaction times were slow. With Calmagite rapid colour changes, within 15 minutes, were found when the dye was deposited on to polyvinyl alcohol (PVA) polymer which had been coated onto a borosilicate glass plate. However, with Orange G and Orange II the colour changes on the PVA/plates were slow and this may be due to the limited availability of CO_2, as the activating species, in generating $CO_3^{-\bullet}$.

Introduction

Peroxide based explosives (PBEs) are synthesised from hydrogen peroxide (H_2O_2) and contain peroxide linkages incorporated within a cyclic carbon structure such that the scaffolding holds the reacting atoms in close proximity to each other. This is shown in the structures (Fig. 1) of triacetone triperoxide (TATP) and hexamethylene triperoxide diamine (HMTD).
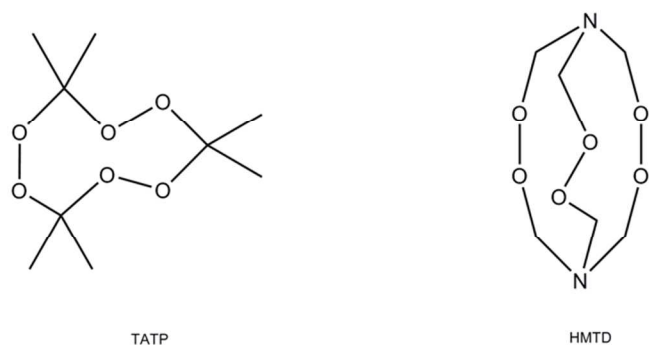

TATP   HMTD

Fig. 1 The structures of TATP and HMTD.

The explosive nature of PBEs is associated with the weakness of peroxide bonds (ΔH_{bond} (O–O) = 147 kJ mol^{-1}) giving spin-allowed reactions under ambient conditions hence, unlike reactions of O_2, activation energies are low, and the heat generated in producing large volumes of thermodynamically stable gaseous products (CO_2, H_2O, acetone *etc*).[1,2] The explosive power of TATP has been described as an "entropic burst" but the negative enthalpy of this reaction cannot also be ignored which together generate large amounts of free energy that leads to rapid acceleration in reaction rates resulting in an explosive power comparable to that of TNT.[3]

It is reported that PBEs were first used in 1980[4] but have gained notoriety in their more recent uses including the Casablanca explosions in 2003[5], the London public transportation attacks in 2005[6] and the transatlantic flight bombing attempt in 2006[5]. These events draw attention to the need for reliable and selective detection methods for PBEs. The ready availability of the simple chemicals required to manufacture PBEs and the relative ease of their syntheses allow for the clandestine manufacture of such explosives using "kitchen sink" methodologies. For example, H_2O_2 is used in hair and teeth bleaching, cleaning products and disinfectants, sulfuric acid is used as a household drain cleaner and acetone as nail varnish remover. Indeed there are concerns that TATP can be assembled from these innocuous precursor chemicals at the target site.

As well as their ease of manufacture, PBEs are very difficult to detect because they lack a nitro (NO_2) group which by contrast makes nitro-based explosives (NBEs) easy to detect by mass spectrometry, and they also lack absorbance in the UV. Several detection methods for PBEs and H_2O_2 have been described in a review by Burks and Hage.[4] These include colorimetric, spectroscopic (IR, Raman, luminescence, fluorescence) and electrochemical methods. However, these techniques are more suited to laboratories and the authors emphasised the need for portable or handheld devices such as test strips for the field detection of PBEs and their precursors. PBEs are volatile and generate a high vapour pressure[7] under ambient conditions and therefore detection methods can be developed to detect H_2O_2 in the vapour, with the use of trained sniffer dogs being reported[8]. Simple portable devices that are selective and sensitive to H_2O_2 vapour would be ideal for the rapid detection of PBEs at public places like airports and train stations.

Progress in the development of rapid colorimetric methods for the detection of H_2O_2 vapours have been made by Mills[9] and Suslick[10]. Mills used a single green/blue azo dye Lissamine Green (LG) dissolved in polyvinyl alcohol (PVA) which was rapidly bleached in the presence of H_2O_2 vapours. However, chlorine (Cl_2), nitrogen dioxide (NO_2) and ozone (O_3) also produced bleaching of LG indicating non-selectivity to H_2O_2. By using a combination of sixteen dyes in an array, Suslick was able to show selectivity to H_2O_2 vapours with detection limits below 2 ppb. However, a flatbed scanner is needed to analyse

the array and the need for so many dye formulations is also undesirable.

The bleaching of the azo dyes Calmagite, Orange G and Orange II using in situ generated H_2O_2 has been described.[11] These results show that at pH 8.0, the *o,o*-dihydroxy dye Calmagite is rapidly bleached but the monohydroxy azo dyes Orange II and Orange G (Fig. 2) are not bleached, or their reactions are very slow.
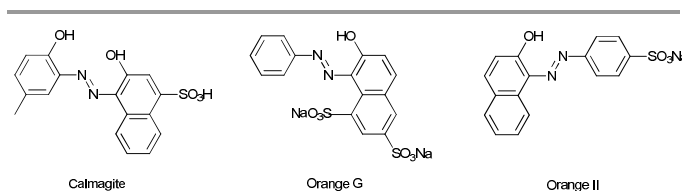

Fig. 2 The structures of Calmagite, Orange G and Orange II.

When using added H_2O_2, Orange G and Orange II are rapidly bleached at pH 9.0 in the presence of added sodium carbonate (Na_2CO_3). It has been suggested that this is due to the in situ generated peroxycarbonate ion (HCO_4^-), a more potent oxidising agent[12–14], formed (equation (1)) from the reaction of H_2O_2 with bicarbonate (HCO_3^-).

$$H_2O_2 + HCO_3^- \rightarrow HCO_4^- + H_2O \qquad (1)$$
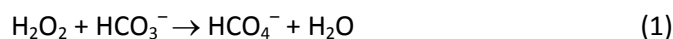
However, Fridovich[15] argues that it is CO_2 and not HCO_3^- that is the enhancing species and that it is the carbonate radical ($CO_3^{-\bullet}$) not HCO_4^- that is responsible for the oxidative degradation of the dye. This work provides some evidence to support the involvement of $CO_2/CO_3^{-\bullet}$. In any case, it should be possible to selectively detect H_2O_2 vapours from a suitable combination of the bleaching of Calmagite at pH 8.0 (EPPS), and Orange G and Orange II at pH 9.0 (Na_2CO_3), with a lack of bleaching of Orange G and Orange II at pH 8.0 (EPPS), especially in the presence of the complexing agent ethylenediaminetetraacetic acid (H_4edta). In the case of Cl_2, NO_2 and O_3, no discrimination would be expected thus providing selectivity to H_2O_2 and PBE vapours. These colour tests can be used in combination with the use of aqueous, acidified, titanium(IV) which is known to form a bright yellow-orange coloured complex[16], $[Ti(O_2)(OH)(H_2O)_3]^+$ with solutions containing H_2O_2 (equation 2) due to a ligand-to-metal charge transfer (LMCT)[17].

$$[Ti(OH)_3(H_2O)_3]^+ + H_2O_2 \rightarrow [Ti(O_2)OH(H_2O)_3]^+ + 2\ H_2O \quad (2)$$

Experimental

Materials

All the reagents used were purchased from Sigma-Aldrich. The polymer used to make the ink films was poly(vinyl alcohol) [PVA, M_w 146,000-186,000, 99+% hydrolysed]. Square (22 mm) borosilicate glass plates were used to provide a transparent

substrate for the inks. De-ionised water (ELGA Purelab) was used in all experiments. Filter papers were purchased from Whatman (No. 1). Hydrogen peroxide solutions were prepared from the dilution of 30%(*w/w*) aqueous H_2O_2 stock solutions. Aqueous titanium (IV) in sulfuric acid (10%) was prepared according to reported methods.[18] Nitrogen dioxide was generated by the dropwise addition of concentrated HNO_3 onto copper turnings while chlorine gases was generated by the dropwise addition of concentrated HCl on to MnO_2; ozone was generated via an O_2 cylinder using a Wallace & Tiernan Type BA.023 laboratory ozonator with the voltage set at 200 V and with O_2 gas at a flow rate of 150 L hr^{-1}. All three gases were separately fed into desiccators containing filter papers or ink coated plates.

Preparation of inks and plates

PVA crystals (10 g) were dissolved in water (90 mL) at 90°C, cooled to room temperature and stirred overnight. For filter paper studies the dye inks were prepared by making up 10.0 mM aqueous solutions of the different dyes and then mixing aliquots (4.00 mL) with either aqueous manganese(II) chloride tetrahydrate ($MnCl_2 \cdot 4H_2O$, 5.00 mM, 1.00 mL) or ethylene diamine tetraacetic acid (H_4edta, 1.00 mM, taken to pH 7 using aqueous NaOH), EPPS (*N*-2-hydroxyethyl-piperazine-*N'*-3-propanesulfonic acid, 0.50 M, taken to pH 8.0 using aqueous NaOH) or sodium carbonate (0.50 M, taken to pH 9.0 using aqueous HCl) and ethanol (1.00 mL). Dye solutions were spotted on to filter papers which were then dried in a desiccator before use. For ink films, the above procedure was repeated except that 0.10 mmol of solid dye was used *e.g.* for Calmagite 0.0358 g of the dye was used. The PVA and inks were then cast onto the glass plates using a spin coater. A few drops of the PVA solution were deposited on to the surface of the plate which was then spun at 2400 rpm for 25 s, then a few drops of the ink solution were added onto the PVA layer and the plate spun again at 2400 rpm for 25 s. The substrate was dried using a stream of hot air from a hair dryer for 30 s and allowed to cool to room temperature before use. The dye/PVA plates were stored in a desiccator under ambient conditions.

The methodology adopted of coating PVA first on to glass plates and then the dye inks onto PVA was adopted because when solid Calmagite was added to the PVA solution (using the method by Mills[9]), the ink would solidify immediately which made application of the ink to the glass plates very difficult. As soon as both layers were applied they mixed naturally. Dissolving the dye in aqueous solution first and then mixing it with the PVA also worked. All three methods were tried and gave comparable results. Keeping the dye solution and PVA separate meant a much longer shelf life for the ink components.

UV–visible spectrometry

Spectroscopic measurements were made using a Jenway 7315 scanning spectrophotometer with the filter papers or plates attached to the cuvette holder using blue tac. For kinetic measurements a 1 cm plastic cuvette was used into which were drilled two 2 mm holes at a vertical separation of 3 mm along the centre of the cell and ~10 mm above the base. The base of the cell was filled with aqueous H_2O_2 and the PVA/dye plates were attached to the cuvette holder facing inwards so that they could be exposed to the H_2O_2 vapours exiting the cuvette through the drilled holes. The cuvette was capped and a tight seal all the way around the plate and the cuvette holder was achieved using a flat layer of blue tac attached to the holder. In this way all the H_2O_2 vapours would be exposed only to the plate. Before each experiment, the aqueous H_2O_2 in the well of the cuvette was allowed to equilibrate with its headspace. Under these conditions the vapour pressure of the H_2O_2, pH_2O_2, is directly proportional to the concentration of H_2O_2 in solution.[19]

Results and discussion

Bleaching of azo dyes in aqueous solution

It has been previously[11] shown that Calmagite is rapidly bleached at pH 8.0 (EPPS, N-2-hydroxyethylpiperazine-N'-3-propanesulphonic acid, 50.0 mM) by in situ generated H_2O_2 from the manganese (II) catalysed reduction of O_2. However, under these conditions, neither Orange G (O G) nor Orange II (O II) is bleached rapidly. These results can be repeated using added H_2O_2. Fig. 3 (left) shows the dark purple colour of an aqueous solution of Calmagite (0.100 mM) at pH 8.0 (EPPS) and the disappearance of the colour after ~30 min in the presence of added H_2O_2 (50.0 mM) and aqueous Mn^{2+} (5.00 μM) as catalyst. Fig. 3 (right) shows that while both O G and O II are bleached at pH 9.0 (Na_2CO_3), neither are perceptibly bleached at pH 8.0 (EPPS).
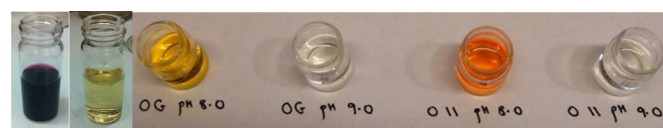

Fig. 3 (left) Aqueous Calmagite (0.100 mM) at pH 8.0 (EPPS, N-2-hydroxyethylpiperazine-N'-3-propanesulphonic acid, 50 mM) before (purple) and after (pale yellow) addition of H_2O_2 (50.0 mM) and aqueous Mn^{2+} (5.00 μM).

Fig. 3 (right) Aqueous Orange G and Orange II at pH 8.0 (EPPS, N-2-hydroxyethylpiperazine-N'-3-propanesulphonic acid, 50 mM), and Orange G and Orange II at pH 9.0 (sodium carbonate, 50 mM) after the addition of H_2O_2 (50.0 mM) and aqueous Mn^{2+} (5.00 μM).

This would form the basis for the selective detection of H_2O_2 vapours as the rationale is that only in the presence of H_2O_2 can HCO_4^- or $CO_3^{-\bullet}$ be generated in situ and this is required for the oxidative degradation of O G and O II. It should also be noted that the rate of bleaching of O G and O II in the presence of

sodium carbonate (Na_2CO_3) is pH dependent, with the rate of bleaching at pH 8.0 being very slow.

Visual Filter Paper Tests Using Vapours

Fig. 4 shows the colours of filter papers coated with Calmagite at pH 8.0 (dark purple), O G at pH 8.0 and pH 9.0 (yellow-orange), O II at pH 8.0 and pH 9.0 (dark orange) and Ti(IV) (colourless) before exposure to any vapours.
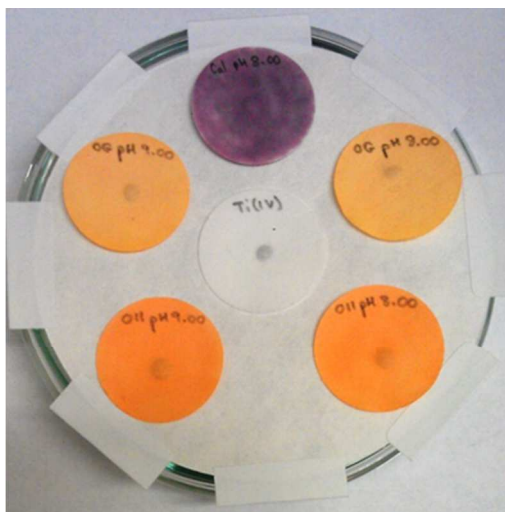

Fig. 4 Filter papers coated with azo dyes or aqueous Ti(IV) before exposure to H_2O_2 vapours. From top (clockwise): Calmagite at pH 8.0, Orange G at pH 8.0, Orange II at pH 8.0, Orange II at pH 9.0, Orange G at pH 9.0. Centre: Ti(IV).

After exposure to H_2O_2 vapours from solutions containing 0.50 M and 5.0 M H_2O_2 for 24 hr (Fig. 5) under ambient conditions, the Calmagite disks were almost completely bleached (purple to pale pink), the O G pH 9.0 disks were completely bleached (yellow-orange to colourless) and the O II pH 9.0 disks were partially bleached (dark orange to light orange), with the 5.0 M H_2O_2 vapour disk exhibiting more bleaching than the one exposed to 0.50 M H_2O_2. In contrast, the O G and O II disks at pH 8.0 showed no bleaching.
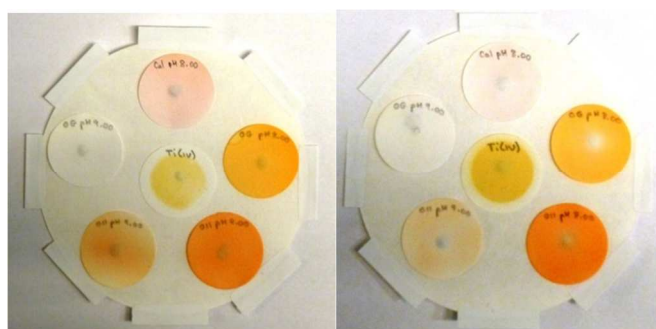

Fig. 5 Filter papers coated with azo dyes or aqueous Ti(IV) after exposure to 0.50 M (left) or 5.0 M (right) H_2O_2 vapours. From top (clockwise): Calmagite at pH 8.0, Orange G at pH 8.0, Orange II at pH 8.0, Orange II at pH 9.0, Orange G at pH 9.0. Centre: Ti(IV).

Control experiments with pure water rather than aqueous H_2O_2 showed no bleaching of any of the disks indicating that

bleaching was due to H_2O_2 vapours and not degradation of the dye through environmental exposure. These results are consistent with the aqueous solution studies and indicate pH selective bleaching of the O G and O II azo dyes which in combination with the bleaching of Calmagite and the formation of a yellow colour (Fig. 5, centre) of $[Ti(O_2)OH(H_2O)_3]^+$ peroxo complex with Ti(IV) provide a potentially useful way to distinguish H_2O_2 vapours from other chemical vapours.

Fig. 6 shows the effect of exposure of the filter papers to $Cl_2(g)$, $NO_2(g)$ and $O_3(g)$ for 24 hr under ambient conditions.
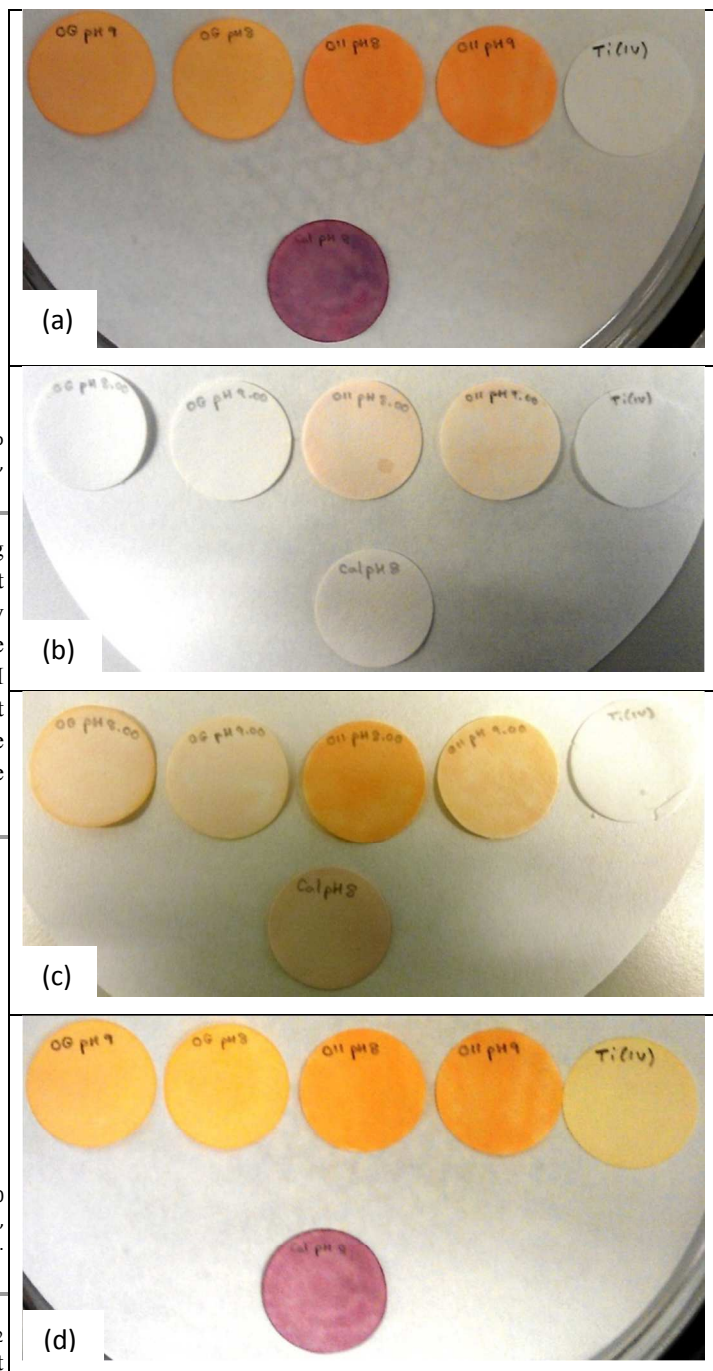
Fig. 6 Filter papers coated azo dyes or aqueous Ti(IV) before exposure (a) or after exposure to (b) $Cl_2(g)$, (c) $NO_2(g)$ and (d) $O_3(g)$. From left to right (in each row): Orange G at pH 8.0, Orange G at pH 9.0, Orange II at pH 8.0, Orange II at pH 9.0 and Ti(IV). Bottom row: Calmagite at pH 8.0.

It is immediately clear the bleaching results are very different to those with H_2O_2 vapours. With $Cl_2(g)$ all the azo dye disks are fully bleached, with the exception of O II at pH 8.0 and pH 9.0 which are ~95% bleached and no reaction with Ti(IV) is discernible. In the case of $NO_2(g)$, all the azo dye disks are partially bleached with the exception of O II at pH 8.0 where there appears to be only partial bleaching and again there appears to be no reaction with Ti(IV). Lastly, with $O_3(g)$ there is only partial bleaching of the azo dyes (with the change of Calmagite being the most distinctive) and with the Ti(IV) disk there is a definite yellowing which could in isolation give a false positive for H_2O_2 vapours. This may be caused by the formation of a Ti(IV)-O_3 complex which is also yellow or the catalysed reduction of O_3 to H_2O_2, with the subsequent formation of the Ti(IV)-peroxo complex (equation (2)). These somewhat surprising results with O_3 were reproducible.

The sensitivity of Ti(IV) to aqueous H_2O_2 and H_2O_2 vapours is shown in Fig. 7 where concentrations as low as 0.010 M (~3 ppm) can be detected and may be used to estimate the concentration of H_2O_2 vapour.
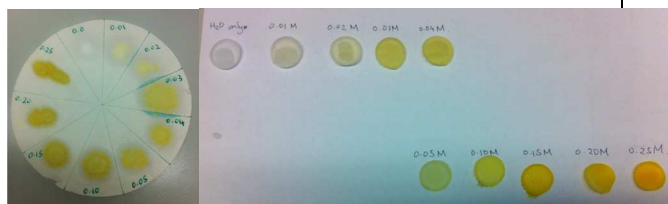

Fig. 7 Filter paper (left) soaked with aqueous Ti(IV) and then dried with the addition of either deionised water ('0.0') or different aqueous $[H_2O_2]$ ('0.01' to '0.25' M) or filter paper discs (right) soaked with Ti(IV) and then dried and placed over sample vials containing either deionised water ('H_2O only') or different aqueous $[H_2O_2]$ ('0.01' to '0.25' M).

Visual Film Tests Using Vapours

In general faster response times were obtained when the dye and Ti(IV) substrates were coated as ink films onto PVA coated borosilicates plates that were placed on top of vials containing 5.0 M (~15%) solutions of H_2O_2 (Fig. 8, *two column, see end of manuscript*). Calmagite at pH 8.0 is visibly bleached within 15 min (indeed changes are observed within the first 5 min). This increase in reactivity can be attributed to a positive change in the microenvironment polarity when the dye is encapsulated in a PVA film.[9] However, the changes in colour for O G and O II on PVA are not similarly quickened. At pH 9.0 O G appears to go a mottled or speckled orange, which gives an indication of a reaction before bleaching completely within 24 hr. In contrast O G at pH 8.0 shows no change over a 24 hr period. The colour changes for O II are less visually clear but there is some bleaching between 15 min and the end of the test period at pH 9.0 while at pH 8.0 there is no change at 15 min. The Ti(IV)

plate showed a clear yellowing of the film with within 15 min, indicating the presence of H_2O_2 vapours.

These experiments were repeated using $Cl_2(g)$, $NO_2(g)$ and $O_3(g)$ (Fig. 9).
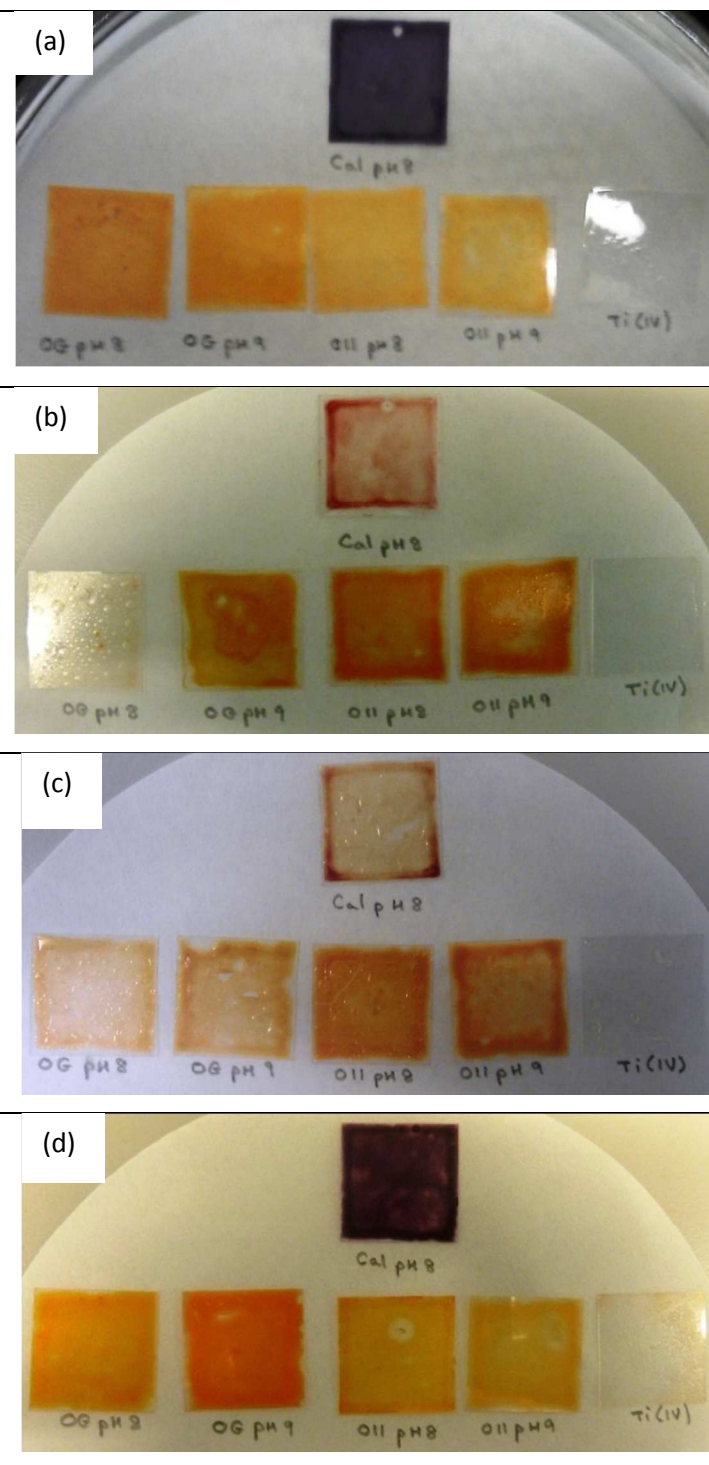

Fig. 9 Images of films (a) before and after exposure to vapours from (b) $Cl_2(g)$, (c) $NO_2(g)$ and (d) $O_3(g)$.

Again it is clear that results with these three gases are very different to those of H_2O_2. The most dramatic dye bleaching is observed with $NO_2(g)$, with no change in the Ti(IV) film. Most surprisingly, $O_3(g)$ shows virtually no bleaching of the azo dyes but there is a colourisation of the Ti(IV) plate suggesting that the yellowing of Ti(IV) is not selective to H_2O_2. In the case of $Cl_2(g)$ rapid bleaching of Calmagite and O G at pH 8.0 is observed, while the bleaching of the other azo dyes is much slower, with no change in colour of the Ti(IV) plate.

Spectral Studies Using Vapours

To enable a quantitative basis for visual studies and to enable the possible use of electronic devices to be combined with the changes in the colour of films, visible spectra (nominally 400 – 800 nm) were recorded before, after and, if appropriate, during the changes occurring on the films. These spectra are displayed in Figs. 10 – 15 and confirm the visual results from both the filter paper and film tests - with the exception of the bleaching of O II at pH 9.0 (Fig. 14) where little change in absorbance over a period of 90 minutes was observed.
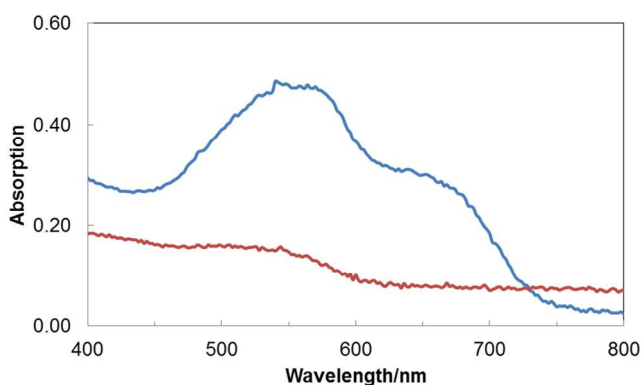
Fig. 10 The absorption spectrum of a Calmagite film at pH 8.0 before (blue) and after (red) exposure to vapours for 10 min from a 5.0 M (~15 %) aqueous solution of H_2O_2.
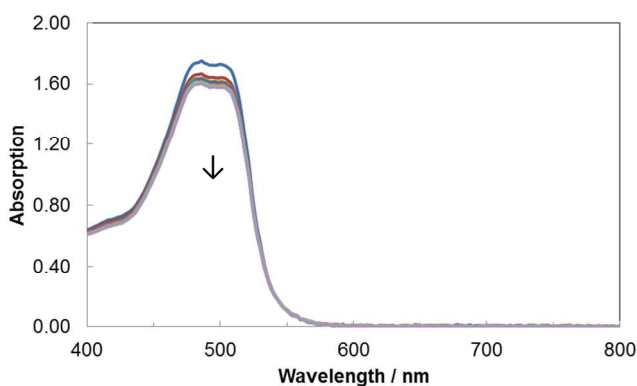
Fig. 11 The absorption spectrum of a Orange G film at pH 8.0 during exposure to vapours at 10 min intervals from a 5.0 M (~15 %) aqueous solution of H_2O_2.

Fig. 12 The absorption spectrum of an Orange G film at pH 9.0 during exposure to vapours at 10 min intervals from a 5.0 M (~15 %) aqueous solution of H_2O_2.

Fig. 13 The absorption spectrum of an Orange II film at pH 8.0 during exposure to vapours at 10 min intervals from a 5.0 M (~15 %) aqueous solution of H_2O_2.
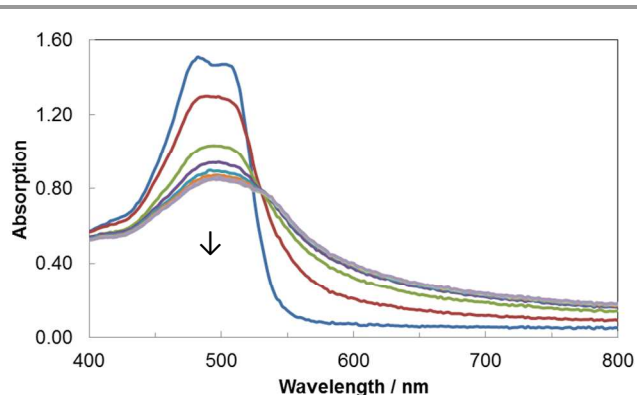
Fig. 14 The absorption spectrum of an Orange II film at pH 9.0 during exposure to vapours at 10 min intervals from a 5.0 M (~15 %) aqueous solution of H_2O_2.
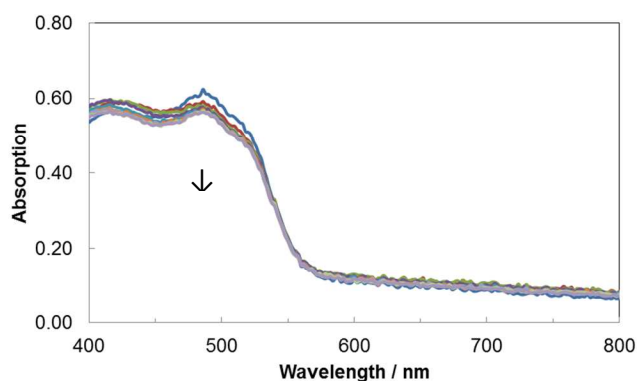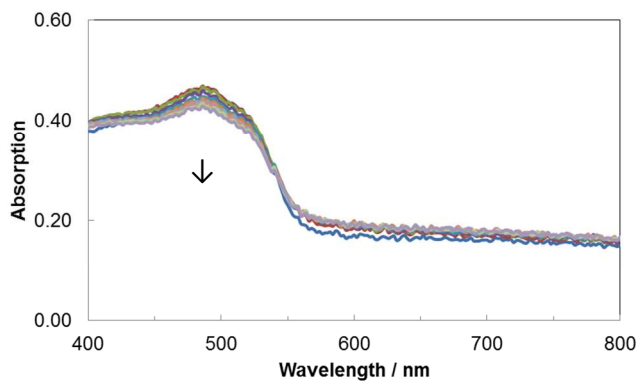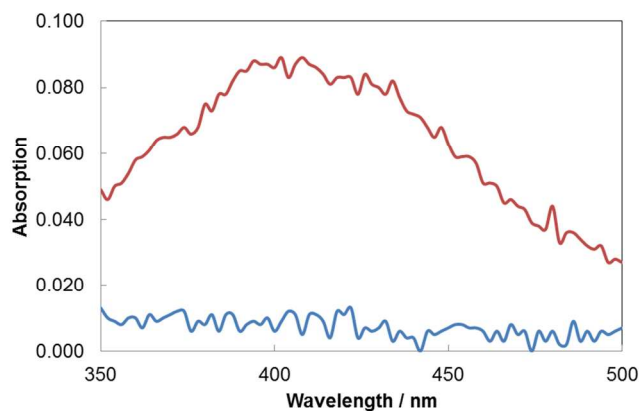
Fig. 15 Normalised absorption spectrum of a Ti(IV) film before (blue) and after (red) exposure to vapours from a 5.0 M (~15 %) aqueous solution of H_2O_2.

Fig. 16 shows that oxidative degradation of O II at pH 9.0 as measured by its change in absorbance at 490 nm does occur on the film but the reaction is very slow with a change of only ~0.04 absorbance units over this period. This spectral data supports the visual tests on the O II pH 9.0 film. It is clear, as stated earlier, that for this particular substrate (and perhaps to a lesser extent O G), the PVA/plate appears to have an inhibitory effect on the reaction of H_2O_2 vapours with the dye substrates.
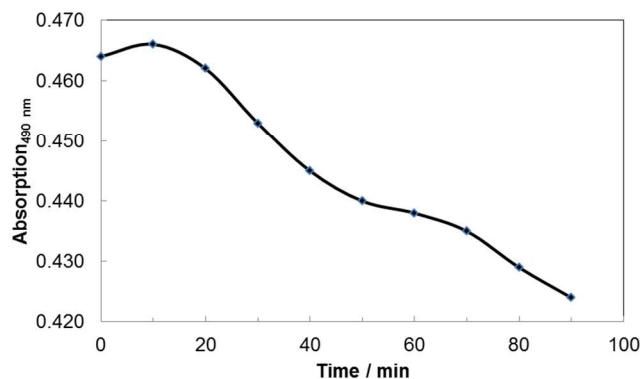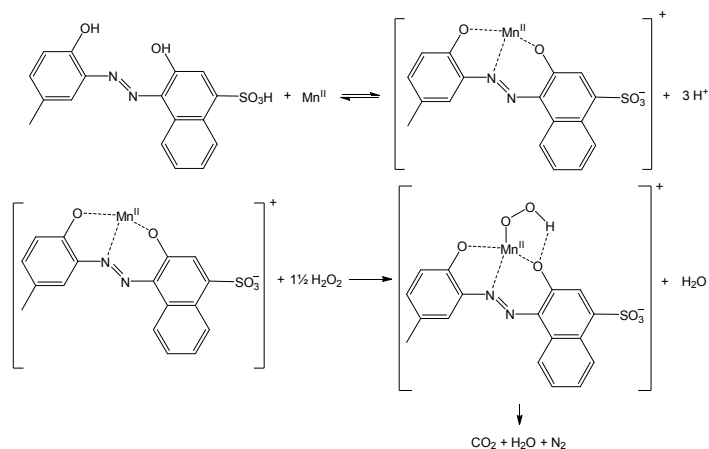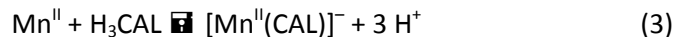

Fig. 16 A plot of ΔAbs_{490} against time for the Orange II film at pH 9.0 during exposure to vapours from a 5.0 M (~15 %) aqueous solution of H_2O_2.

The most rapid (within 5 min) and distinctive bleaching is with the dark purple Calmagite dye and this in itself provides a rapid (but non-selective) indication of the presence of oxidising vapours.
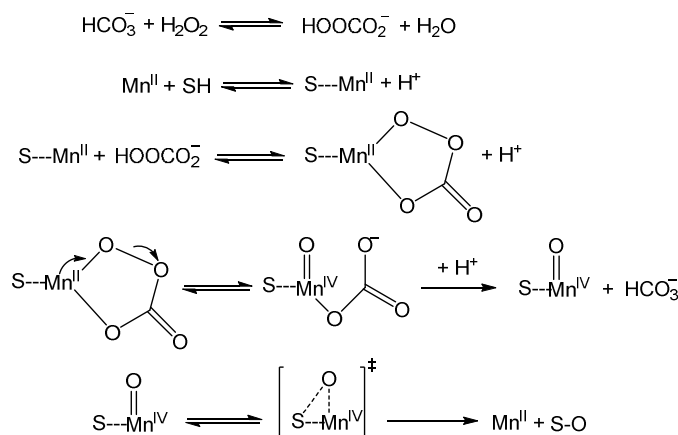
Mechanisms of Dye Bleaching

The bleaching of Calmagite at pH 8.0 (EPPS) is fast and requires less aggressive oxidative conditions than O G and O II with carbonate not being required to achieve oxidative degradation. This may be related to the greater coordinating properties of Calmagite that has a *o,o*-dihydroxy motif enabling it to act as a tridentate ligand to a metal centre, compared to O

G and O II that can only bind in a bidentate fashion. A mechanism for Calmagite bleaching can be proposed of the attack of coordinated of hydroperoxo ion (O_2H^-) on coordinated Calmagite (equations (3) – (5) and Scheme 1).

$$Mn^{II} + H_3CAL \ \rightleftharpoons \ [Mn^{II}(CAL)]^- + 3\ H^+ \qquad (3)$$

$$[Mn^{II}(CAL)]^- + 1\tfrac{1}{2}\ H_2O_2 \rightarrow [Mn^{III}(CAL)(O_2H)]^- + H_2O \qquad (4)$$

$$[Mn^{III}(CAL)(O_2H)]^- \rightarrow \text{oxidised CAL} \rightarrow CO_2 + H_2O + N_2 \qquad (5)$$

Scheme 1 The manganese catalysed oxidative degradation of Calmagite by H_2O_2 vapours.

This is similar to the mechanism proposed for the oxidative degradation of Calmagite using in situ generated H_2O_2, where EPR solution studies suggested the presence of Mn^{III} but no Mn^{IV}=O species.[11] Under these conditions (pH 8.0 and in the absence of sodium carbonate), O G and O II are bleached only very slowly, presumably because they only weakly coordinate to Mn^{II}. At pH 9.0 (Na_2CO_3), rapid bleaching of O G and O II was observed in solution and on filter papers but the reactions were more sluggish with the inks coated on to PVA coated borosilicate glass plates. The oxidative degradation of O II by peracetic acid catalysed by the oxo-bridged $[Mn_2^{III/IV}(\mu\text{-}O)_2(bpy)_4](ClO_4)_3$ complex and its mononuclear analogue $[Mn^{II}(bpy)_2Cl_2]$ have been studied by van Eldik *et al*. who proposed that the reaction proceeds via the in situ formation of $HCO_4^-/HOOCO_2^-$ which on coordination to Mn^{II} results in the formation of Mn^{IV}=O (Scheme 2).[14] In this proposed mechanism there is a requirement for at least weak binding of O II to the manganese centre to effect its oxidative degradation.

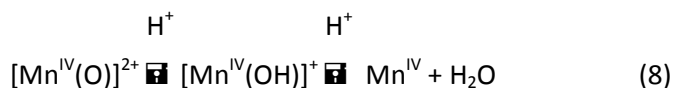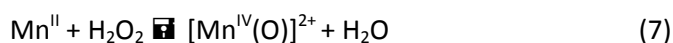$$HCO_3^- + H_2O_2 \rightleftharpoons HOOCO_2^- + H_2O$$

$$Mn^{II} + SH \rightleftharpoons S\text{---}Mn^{II} + H^+$$

$$S\text{---}Mn^{II} + HOOCO_2^- \rightleftharpoons S\text{---}Mn^{II}(O_2CO) + H^+$$

(Scheme 2 reaction mechanism with Mn species)

$$S\text{---}Mn^{II} \rightleftharpoons S\text{---}Mn^{IV}(CO_3) \xrightarrow{+H^+} S\text{---}Mn^{IV} + HCO_3^-$$

$$S\text{---}Mn^{IV} \rightleftharpoons [S\text{---}Mn^{IV}(O)]^{\ddagger} \longrightarrow Mn^{II} + S\text{-}O$$

Scheme 2 Mechanism proposed by van Eldik *et al.* for the Mn^{II} catalysed oxidative degradation of Orange II (SH) by H_2O_2 in the presence of carbonate buffer at pH 8-9.

Yin has proposed a different mechanism for the HCO_3^- activated H_2O_2 oxidative degradation of methylene blue using supported Co^{II} that involves the carbonate radical $(CO_3^{-\bullet})$ and possibly singlet dioxygen $(^1O_2)$.[20] The involvement of the $CO_3^{-\bullet}$ is also supported by Fridovich in which the terminal step would involve a one-electron oxidation of the organic substrate (SH) leading to its oxidative decomposition (equation (6)).[15]

$$CO_3^{-\bullet} + SH \rightarrow HCO_3^- + S^\bullet (\rightarrow CO_2 + H_2O + N_2) \quad (6)$$
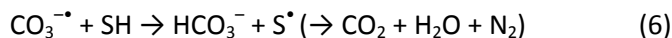
While the formation of $CO_3^{-\bullet}$ can be thought to be easily generated from the one-electron oxidation of HCO_3^- coordinated to Mn^{III} or Mn^{IV} species, Fridovich intriguingly suggests that the presence of CO_2 may enhance the Mn^{II} catalysed peroxidation of a substrates by the following mechanism (equations (7) – (10)).

$$Mn^{II} + H_2O_2 \rightleftharpoons [Mn^{IV}(O)]^{2+} + H_2O \quad (7)$$

$$[Mn^{IV}(O)]^{2+} \underset{\quad}{\overset{H^+}{\rightleftharpoons}} [Mn^{IV}(OH)]^+ \underset{\quad}{\overset{H^+}{\rightleftharpoons}} Mn^{IV} + H_2O \quad (8)$$

$$Mn^{IV} + CO_2 \rightleftharpoons Mn^{III} + CO_2^+ \quad (9)$$

$$CO_2^+ + HO^- \rightleftharpoons CO_3^{-\bullet} + H^+ \quad (10)$$

It can be argued that the presence of CO_2 displaces the equilibrium of reaction (7) to the right by consuming $[Mn^{IV}(O)]^{2+}$ and this enhances the rates of consumption of both Mn^{II} and H_2O_2 and regenerates Mn^{III}. While it may seem strange that CO_2 is more readily oxidised than HCO_3^-, Fridovich argues that as well as an uncharged linear molecule, an alternative resonance form that can exist for CO_2 is one with one oxygen atom positive and the other negative (Scheme 3).[21]

$$O=C=O \longleftrightarrow {}^+O\equiv C\text{--}O^- \longleftrightarrow {}^-O\text{--}C\equiv O^+$$
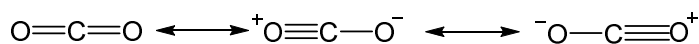
Scheme 3 Resonance forms for CO_2.

In this case the loss of an electron from the negative oxygen atom yields CO_2^+ and this may explain why CO_2 is more readily oxidised than HCO_3^-. This result would explain the sluggish bleaching of O G and especially O II inks deposited on an impermeable PVA/borosilicate plate, which is somewhat off-set by the favourable polar environment created by the PVA, while on porous filter paper the reactions are slow but not inhibited.

Conclusions

The colour test results from exposure to H_2O_2 vapours are distinctive from the results obtained with Cl_2, NO_2 and O_3 giving general selectivity to H_2O_2. While the formation of $[Ti(O_2)OH(H_2O)_3]^+$ with Ti(IV) provides a sensitive colour test for H_2O_2 vapours it cannot be used in isolation since $O_3(g)$ also produces a yellowing of the Ti(IV) film. The difference in reaction of H_2O_2 vapours to O G and O II at pH 8.0 compared to that pH 9.0 on filter papers provide for a selective method for the detection of H_2O_2 vapours. As such this work provides an advance on the system described by Mills *et al* using LG where no discrimination between H_2O_2, Cl_2, NO_2 and O_3 was reported.[9] Indeed the use of Ti(IV) with just O G at pH 8.0 and pH 9.0 would be sufficient to positively identify H_2O_2 vapours from Cl_2, NO_2 and O_3 since only H_2O_2 and O_3 produce a yellowing of Ti(IV) but it is only H_2O_2 that induces a degradation of O G at pH 9.0. The inclusion of Calmagite or indeed LG in any detector system would be useful as they generate the most rapid and visually distinctive colour changes and so provide a fast and clear indication of the presence of an oxidising vapour.

More work is needed to produce a commercially viable system, especially in making the colour change with O G and especially O II at pH 9.0 clearer and more rapid, while also attempting to completely inhibit the reactions at pH 8.0. From both a theoretical and practical point of view, it would also be useful to investigate the role of CO_2 in the reactions of O G and especially O II at pH 9.0. The use of O II being a much darker shade of orange this could potentially be a more useful dye to use than O G in any detection system. One attractive feature of this method is the inexpensive materials that are used and the ease of making the substrate solutions and inks. Indeed, work in these laboratories has shown that EPPS buffer, a somewhat expensive biological buffer, can be replaced by phosphate buffer for the pH 8.0 dye solutions, thus reducing the cost even further.

Notes

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x

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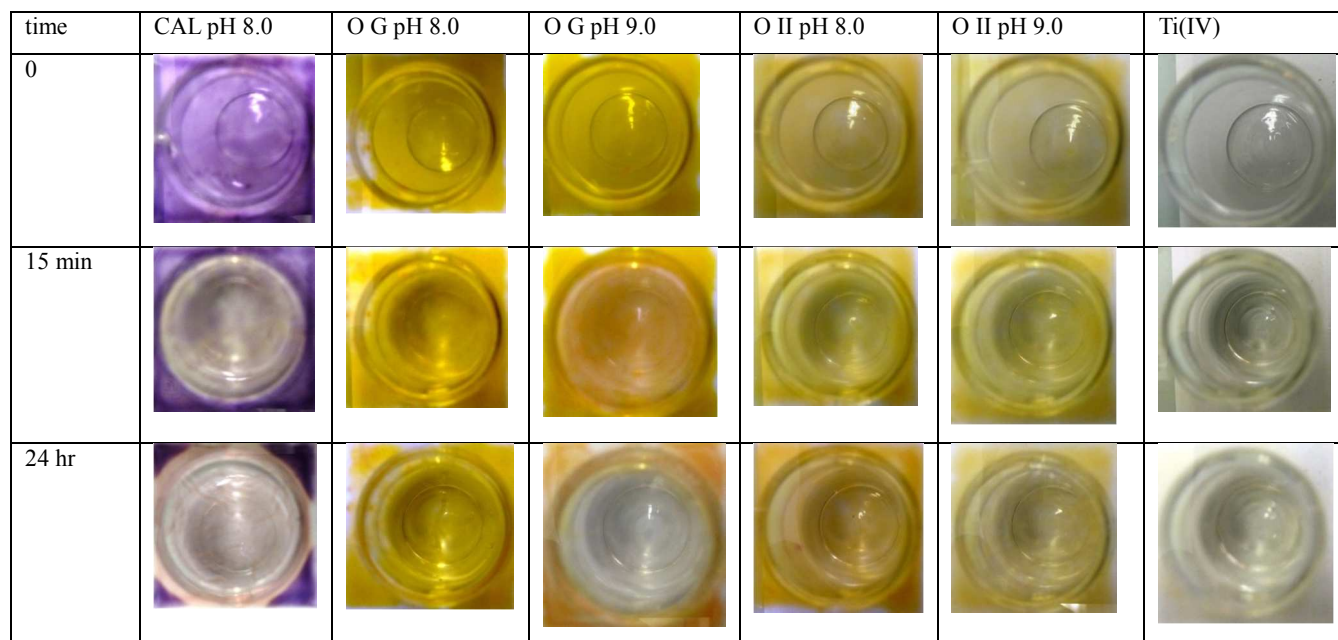21 T. Moeller, *Inorganic Chemistry: An Advanced Textbook*, Wiley, New York, 1964, p. 689.

time	CAL pH 8.0	O G pH 8.0	O G pH 9.0	O II pH 8.0	O II pH 9.0	Ti(IV)
0						
15 min						
24 hr						

Fig. 8 Images of films after exposure to vapours from 5.0 M (~15 %) aqueous solutions of H_2O_2.

Selective Detection of Hydrogen Peroxide Vapours Using Azo Dyes

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A selective visual colour method is described for the discrimination of H_2O_2 vapours *e.g.* from peroxide based explosives from other oxidising vapours such as $Cl_2(g)$, $NO_2(g)$ and $O_3(g)$.