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Determination of Peroxygen Species Present in Pulp Fiber Matrixes

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A new chromatographic method for the determination of oxidants, such as peroxyborates and peroxides, present in a pulp matrix has been developed. The new method is characterized by its high reproducibility, its low limit of detection, and its high selectivity. Thioanisole (methylphenyl sulfide) is shown to selectively and quantitatively react with oxidants that are present within a pulp matrix. The experimental protocol proposed requires an HPLC system with a normal-phase column. The method allows for the quantitative monitoring of the thioanisole starting material, as well as the products of oxidation, methylphenyl sulfoxide and methylphenyl sulfone. After a 2-day reaction period, the analysis time for a sample is less than 20 min. The detection limit is 2.7×10^{-6} M for the sulfoxide and sulfone and less than 5.0×10^{-7} M for the thioanisole. This novel approach for monitoring oxidants present on solid lignocellulosic matrixes may provide pulp and paper manufacturers with a new tool for the study of the long-term bleaching effectiveness of peroxy-containing chemical additives.

Manufacturers of paper products have an interest in designing bleaching methodologies that retain the whiteness of such materials. Hydrogen peroxide (H_2O_2) is currently widely used as a bleaching agent in the pulp and paper industry since environmental and economic concerns have prompted moves toward elemental chlorine-free (ECF) and totally chlorine-free (TCF) bleaching.[1] Peroxide bleaching has been shown to be effective in the brightening of high-yield (lignin-rich) pulps such as groundwood,[2] thermomechanical pulp (TMP), and chemithermomechanical pulp (CTMP)[3] and in the bleaching of softwood kraft[4] and hardwood kraft pulps.[5] However, for high-yield pulps, the whiteness obtained after bleaching is not permanently retained, as evidenced by the yellowing of old newspapers. Both the pulp bleaching and the yellowing processes are poorly understood since the structure of lignin is complex, and the currently utilized bleaching reagents give rise to a variety of other oxidative species whose reactions may interfere with or occur simultaneously with those of the original bleaching agents.[6]

To date, no method capable of accurately measuring low concentrations of residual peroxy moieties on solid pulp and paper matrixes is available. Traditionally, the method of choice for estimating the amount of peroxide present on a pulp was to measure the residual peroxide remaining in solution at the end of the bleaching process using an iodometric titration.[7] In such methods, it is assumed that all of the peroxide not in the residual solution has reacted with the pulp. The proposed method, however, since it is designed to measure minute amounts of peroxy functionality on solid substrates, does not rely on measuring peroxide residuals in solution. This method determines directly the actual amount of oxidant that is present on the pulp.

Transformation of hydrogen peroxide into other reactive peroxygen compounds has been one of the approaches used to increase the effectiveness of peroxide bleaching.[8] Recent studies have demonstrated the effectiveness and advantages of using boron- and oxygen-containing compounds for the bleaching of softwood kraft pulp[9] and softwood thermomechanical pulps (TMP).[10] Peroxyborate compounds prepared in situ with the addition of hydrogen peroxide to Borax have been found to be useful TMP bleaching agents in long-term irradiation experiments.[11] Peroxyborate compounds are thought to form reversible complexes with pulp fiber matrixes. More specifically, Van den Berg et al.[12] have shown that vicinal diols present in carbohydrates may form reversible trinary complexes with borate compounds and alkaline hydrogen peroxide. It is believed that this reversible complex formation allows peroxyborate species to migrate freely and undergo exchange reactions at different sites within the pulp fiber matrix.

As previously stated, there are, at present, no quantitative protocols for the determination of minute quantities of hydrogen

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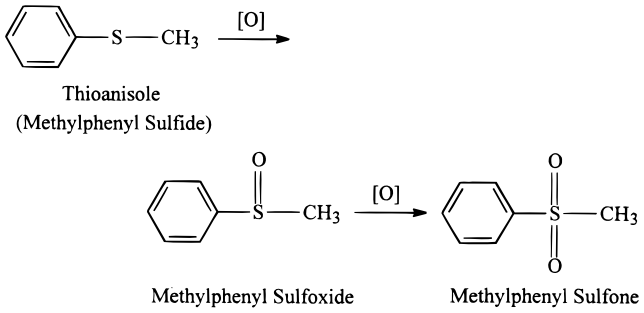
peroxide or other oxidizing species present on solid pulp matrixes. Such a method could be used in determining the type of bleaching process that would be most beneficial for a given pulp and may even provide a better understanding of the precise mechanisms operating during a given pulp bleaching process. The present paper intends to discuss the development of such an analytical protocol.

Thioanisole (methylphenyl sulfide, MPS) has been shown to readily oxidize to methylphenyl sulfoxide (MPSO) in the presence of a small excess of the oxidant sodium perborate, and to methylphenyl sulfone (MPSOO) in the presence of a large excess of sodium perborate.[13,14] This reaction was performed in glacial



acetic acid at the optimized temperature of 50−55 °C, with the products obtained by filtration or solvent extraction and purified by short-column chromatography followed by distillation or crystallization. Utilizing the methodology described by McKillop and Tarbin,[13] it was proposed that in our test procedure, hence known as the thioanisole test, thioanisole would be added to TMP sheets that contain peroxide or peroxyborate compounds, allowing the sulfide to be oxidized to the corresponding sulfoxide or sulfone by reaction with available peroxy or oxidative species within the matrix. HPLC would be used to follow the decrease in the concentration of the thioanisole after reaction with residual oxidant; as well, the corresponding rise in the concentration of oxidation products (sulfoxide and sulfone) would also be monitored.

EXPERIMENTAL SECTION

Chemicals. All chemicals used during this work were commercial products and were used as received. Methylphenyl sulfide (>99%), methylphenyl sulfoxide (>98%), methylphenyl sulfone (>98%), diphenyl sulfone (>97%), ultrapure glacial acetic acid (>99.99%), 30% hydrogen peroxide (reagent grade), sodium perborate tetrahydrate (>97%), and sodium tetraborate decahydrate (Borax) (reagent grade) were purchased from Sigma-Aldrich (Oakville, Canada). HPLC grade ethyl acetate and hexane solvents, reagent grade sodium hydroxide, and laboratory grade sodium chloride were obtained from Fisher (Ottawa, Canada).

Photometer. Ultraviolet spectra were produced using a Lambda 14 (Perkin-Elmer) UV−visible spectrophotometer.

HPLC Apparatus. The high-performance liquid chromatograph used was a Hewlett-Packard 1050 series supplied with a UV variable wavelength detector and a Supelcosil LC-SI, 5-μm, 250- × 4.6-mm normal-phase column.

GC/MS. The gas chromatograph/mass spectrometer consisted of a Hewlett-Packard 5890 GC equipped with a 5972 series mass selective detector.

UV Absorption Measurements. The optimum wavelengths at which the maximum UV absorbance occurred for ethyl acetate solutions of MPS, MPSO, and MPSOO were determined using the UV−vis spectrophotometer. UV spectra were recorded in the scan range of 400−200 nm.

HPLC Analysis. Fifteen microliters of sample was injected directly into the sample loop, with the UV detector set at 265 nm.

Preparation of Pulp Sheets. Black spruce (*Picea mariana*) thermomechanical pulp (TMP) was received from the Pulp and Paper Research Institute of Canada (Pointe Claire, Québec, Canada). Black spruce bleached thermomechanical pulp (BTMP) was prepared from black spruce TMP using 4% H_2O_2 and 2.5% NaOH (charges expressed on oven-dried pulp). TMP and BTMP handsheets were prepared following standard procedures.[15] Brightness values were determined using a Technibrite Micro TB-1C (Technidyne Corp., New Albany, IN). The handsheets were wrapped in aluminum foil and stored in a cool, dark environment until required. All alkaline Borax and/or hydrogen peroxide coating solutions were freshly prepared immediately prior to application on the handsheets. To accurately determine the oven-dried mass of the handsheet material, samples from the same handsheet batch were weighed before and after overnight drying at 110 °C to obtain the moisture content.

Sample Preparation Procedure. The following scheme was devised for the preparation of the thioanisole samples:

(i) The sample to be reacted with the thioanisole was added, along with the appropriate known amount of thioanisole, to glacial acetic acid so that the total volume of the solution was 1.00 mL. If the sample was a solid material, it was cut into pieces of size less than 1 mm^2. The sample and solution were placed in a capped 0.5-dram glass vial.

(ii) The thioanisole was allowed to react with the sample in the glacial acetic acid solution for a period of 2 days (48 h). During this time, the sealed sample was stirred with a magnetic stir bar, with the temperature maintained at 55 °C, using a Pierce Reacti-Therm heating/stirring module.

(iii) After the 48 h mixing and heating period was completed, the sample was removed from the heating and stirring source. For cases where the sample contained solid pulp or paper, the vial was spun at 4400 rpm for 2.5 min in a centrifuge to allow for separation of the solid material from the liquid. A 0.100-mL aliquot was removed from the supernatant and was diluted with ethyl acetate in a 5.00-mL volumetric flask.

(iv) To this ethyl acetate/glacial acetic acid solution was added 1.0 mL of 1 M aqueous sodium hydroxide, to neutralize the acetic acid to a pH of 5−7. The solution was then shaken for approximately 1 min to allow for the neutralization reaction to occur. The solution formed two distinct layers, with the neutralized aqueous layer settling to the bottom of the reaction vessel.

(v) Methylphenyl sulfide, sulfoxide, and sulfone are sparingly water soluble[16] and hence should remain in the organic ethyl acetate layer. However, in the event that trace amounts of these

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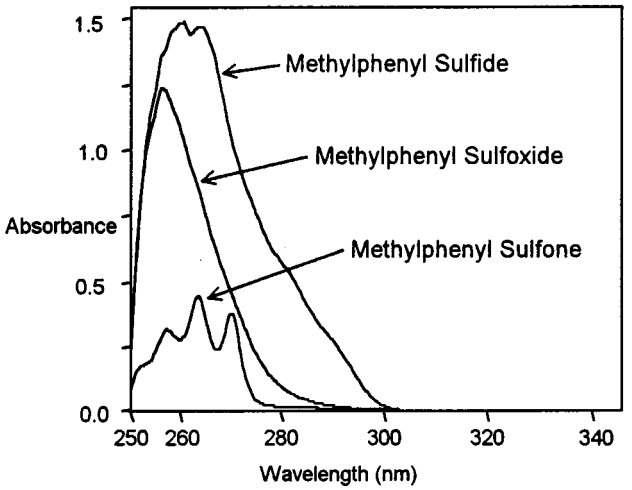

Figure 1. Ultraviolet absorption spectra of methylphenyl sulfide, methylphenyl sulfoxide, and methylphenyl sulfone in ethyl acetate.

compounds would dissolve in the aqueous layer, approximately 2.0 g of sodium chloride was added to "salt-out" the solute from the water. It was later shown that the concentration of the sulfide, sulfoxide, or sulfone was not affected whether the sodium chloride was added or not, although the step of sodium chloride addition was retained in the procedure.

(vi) The organic ethyl acetate layer was then decanted from the lower aqueous layer. A 0.900-mL aliquot was removed, and to this aliquot was added 0.100 mL of the internal standard before injection into the HPLC.

(vii) The sample preparation procedure for the calibration curve solutions was followed as above, except that the heating/stirring step was omitted.

RESULTS AND DISCUSSION

Since the detector present in the HPLC system used for the analysis was a UV detector, the maximum absorbance wavelengths for each of the MPS, MPSO, and MPSOO standards, dissolved in ethyl acetate, were determined using a UV−vis spectrophotometer so as to optimize HPLC integrative analyses. Based on the resulting absorption spectra, maxima were exhibited at 261 nm for MPS, 257 nm for MPSO, and 265 nm for MPSOO (Figure 1). The UV absorption of ethyl acetate could interfere with the spectrometer readings below a wavelength of 265 nm; for this reason, the HPLC−UV detector was set at 265 nm for all further analyses.

Preliminary HPLC trials indicated that standard ethyl acetate solutions of MPS, MPSO, and MPSOO could be adequately separated with a normal-phase column when a mobile phase of 60% ethyl acetate/40% hexane was utilized. To measure the absolute concentrations of MPS, MPSO, and MPSOO, an internal standard had to be added to all samples tested. Diphenyl sulfone (DPSOO) was chosen as a suitable internal standard due to its similar chemical and physical properties to MPS, MPSO, and MPSOO. DPSOO is soluble in ethyl acetate and would not decompose under the experimental conditions or oxidize in the presence of an oxidant. Most importantly, however, the elution of diphenyl sulfone did not interfere with the MPS, MPSO, and MPSOO chromatographic peaks.

A typical chromatographic separation of MPS, MPSO, and MPSOO in the presence of the internal standard DPSOO is shown in Figure 2. Under the operating conditions described, the least polar substance (MPS) eluted first, followed by the two sulfone compounds, and finally by the most polar MPSO. A number of gradient programs were examined in order to minimize the total separation time, but at the low concentrations employed, integration was affected by a shift in the baseline caused by changes in the mobile phase. Subsequent oxidation trials of MPS produced chromatographic oxidation product peaks that corresponded to the standard peaks of MPSO and MPSOO. GC/MS analysis confirmed the identity of each of the standards.

To quantify the amounts of MPS, MPSO, and MPSOO present in a sample, standard solutions of these compounds at various concentrations were analyzed in the presence of 1.00×10^{-3} M diphenyl sulfone, acting as an internal standard. The preparation of these standard solutions was identical to the sample preparation procedure, described in the Experimental Section, except that the heating/stirring step was omitted. The limit of detection for this procedure was determined to be 2.7×10^{-6} M, since this was the detectable concentration for MPSO and MPSOO, although MPS could be detected to concentrations of less than 5.0×10^{-7} M.

Calibrant samples were prepared for each of the MPS, MPSO, and MPSOO in a concentration range of 2.67×10^{-6}−4.50×10^{-4} M in the presence of 1.00×10^{-3} M diphenyl sulfone. For each concentration of the calibrant samples, ratios of the sample peak area to the internal standard peak area were calculated. The resulting peak area ratio versus sample concentrations were linear over the entire range examined, as shown by the correlation coefficients (r^2) values of 0.9995, 0.9982, and 0.9991 for MPS, MPSO, and MPSOO, respectively (Figure 3). In repetitive measurements ($n = 3$), the average standard deviation was less than 2% for each set of the concentration ranges for all three compounds.

In an effort to determine the minimum reaction time required for the complete oxidation of MPS by an oxidant, MPS was reacted with excess hydrogen peroxide following the procedure outlined in the Experimental Section. The solution was analyzed by HPLC at different times (0.1, 1, 2, 3, 4, and 6 days) during the heating/stirring step. The concentration of sulfoxide was found not to increase beyond a 2-day reaction period, within experimental error, based on the original concentration of the hydrogen peroxide, indicating the reaction was complete after a 2-day mixing period. Blank solutions of thioanisole were heated to 55 °C and stirred for 2 days in the absence of any oxidative material to confirm that the MPS would not be converted to MPSO or MPSOO in the presence of glacial acetic acid used as the solvent. MPS was also reacted with TMP and BTMP control handsheets that were not impregnated with hydrogen peroxide. Such samples did not oxidize the MPS over the 2-day test period. Even TMP that was bleached with hydrogen peroxide (BTMP) did not show any oxidizing ability (perhaps in part due to the extended age of the handsheet (>4 months)). These same batches of BTMP were used in all further oxidation experiments.

BTMP handsheets were impregnated with a 3% (by weight) solution of hydrogen peroxide and Borax adjusted to pH 10.8 using sodium hydroxide and stored in the dark under ambient conditions. The 3% (w/w) value was chosen as this would be considered to be approaching the maximum acceptable concentration for an actual industrial process. After an overnight drying period, 25-

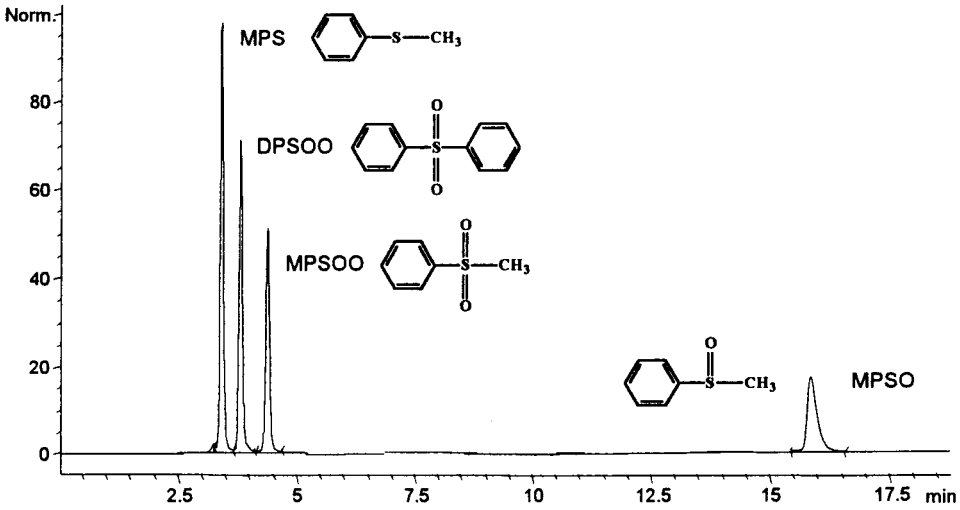

Figure 2. HPLC chromatogram of methylphenyl sulfide (MPS), methylphenyl sulfoxide (MPSO), and methylphenyl sulfone (MPSOO), with diphenyl sulfone (DPSOO) internal standard.

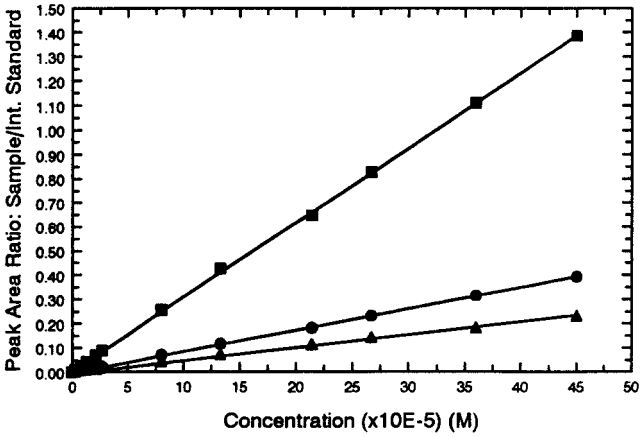

Figure 3. Calibration curves for ethyl acetate solutions of MPS (■), MPSO (●), and MPSOO (▲) in the presence of 1.00 × 10^{-3} M DPSOO.

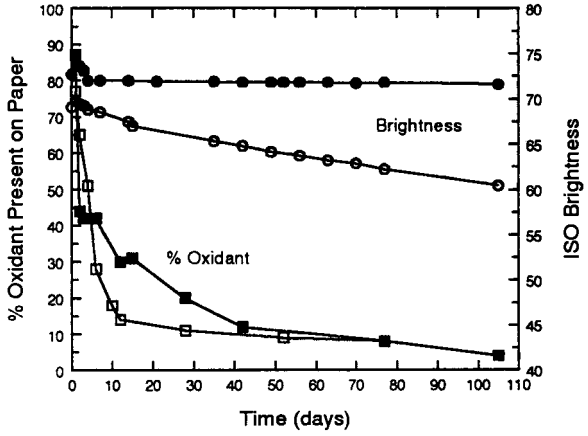

Figure 4. 3% (by weight) H_2O_2 and Borax coatings remaining on BTMP exposed to light (□) and darkness (■) with the corresponding light-exposed ISO brightness (○) and dark-exposed ISO brightness (●) as monitored by reaction with thioanisole.

mg portions of the handsheets were sampled in order to determine the remaining oxidant as a function of time. The amount of thioanisole used at each sampling period was a 1:1 molar equivalent to the maximum amount of hydrogen peroxide that would have been present initially on each 25 mg of the handsheet fiber, in this case 4.0 × 10^{-4} M.

Ideally, the sum of the amounts of methylphenyl sulfide, sulfoxide, and sulfone detected by the HPLC should be equal to the total amount of methylphenyl sulfide that would be present in the original sample, for the present case a concentration of 4.0 × 10^{-4} M. In reality, a variance of up to 5% for this total, due to random electronic instrument response, was observed for repetitive measurements ($n = 3$) for both oxidant-containing sheets and blank controls.[17] For this reason, a total of the methylphenyl sulfide, sulfoxide, and sulfone concentrations for each trial was calculated, and the percentage for each component was determined so as to provide an indication of the degree of oxidation of methylphenyl sulfide. The percentage calculation was performed so as to "normalize" the readings from one time period to the next for a given handsheet sample. For example, due to the random error described above, the total amount of the sulfide/sulfoxide/sulfone would be different even for repetitive measurements of the same sample. It was this percentage value that was compared from one time period to the next, as shown in the following figures. The average standard deviation for the percentage of each component for all samples examined was less than 2%.

As shown in Figure 4, the amount of oxidant present on the fibers steadily decreased over 105 days, as measured by the decreasing concentration of MPSO that was formed after the reaction of thioanisole with the oxidant present on the handsheet fibers. No MPSOO was observed at any time of this or later experiments. The amount of oxidant remaining on the handsheets at various times was correlated with the corresponding ISO brightness. It appeared that even though the oxidant was depleted, if the handsheets were kept in dark storage and not exposed to a light or heat source, the brightness loss was minimal.

The procedure was repeated for a 3% (by weight) charge of hydrogen peroxide/Borax (pH 10.8), with the handsheets exposed to 6 h of fluorescent light followed by 18 h of darkness during each day of a 105-day trial. These conditions were thought to better

(17) Skoog, D. A. *Principles of Instrumental Analysis*, 3rd ed.; Saunders College Publishing: New York, 1985; pp 784−836.

represent common daily handling of paper products. Although the amount of oxidant available on dark storage impregnated BTMP handsheets was marginally greater at any time than the amount of oxidant present on light-exposed handsheets, there was a dramatic difference in the ISO brightness between samples stored in the dark versus those that were exposed to light (Figure 4).

It has been widely recognized for some time that a number of structural changes occur when mechanical pulps, and more specifically the lignin portion of the mechanical pulp fibers, are exposed to light. The presence of alkaline hydrogen peroxide or other peroxy species can retard, alter, or prevent the formation of color-forming moieties in the pulp. Nucleophilic addition of perhydroxyl anions will irreversibly oxidize quinones by ring-opening reactions. In addition, peroxy compounds under alkaline conditions may cause the oxidative elimination of blue light absorbing coniferaldehyde lignin end groups.[6] The addition of alkaline peroxygen species can also lead to the formation of hydroquinone structures, which are not color-causing chromophores. However, hydroquinones, in the presence of a light source, can easily revert back to color-forming structures, thus only delaying the overall color formation in the pulp.[18]

In conjunction with the elimination of certain chromophore groups during peroxide bleaching, competing reactions involving hydroxyl and perhydroxyl ions may lead to the formation of new chromophore systems, which may partially offset the brightness gains resulting from chromophore elimination reactions.[19] These parallel competing reactions are augmented in the presence of a light source. Light-induced brightness reversion studies of mechanical pulps have indicated that chromophoric *o*-quinones and aromatic carbonyl groups are produced, decreasing the brightness of the pulp.[20]

Even when mechanical pulp impregnated with peroxy functionalities is stored in the dark, the reaction of the peroxy groups with the lignin still occurs, resulting in an eventual decrease of oxidant (Figure 4). The presence of transition metals in the pulp, such as iron, manganese, and copper, will cause the destruction of hydrogen peroxide and peroxy moieties,[21,22] providing an explanation for the similar rate of oxidant decrease in both light and dark exposure, as observed in Figure 4. Therefore, the oxidant present on mechanical pulps will react or disappear irrespective of the presence or absence of a light source, and thus, it is not surprising to note similar patterns of oxidant diminution in the dark- and light-exposed thermomechanical pulp, while observing a large difference in the brightness characteristics of the pulp sheets.

The next set of experiments compared the reactivity of 3% (by weight) additives on BTMP of various compounds and combinations of compounds that could be used as potential industrial bleaching agents for TMP or BTMP paper. The chemicals examined were 3% hydrogen peroxide, 3% Borax, 3% hydrogen peroxide with 3% Borax, and 3% sodium perborate (SPB), all at a pH of 10.8. Once the solutions were prepared, they were impregnated on the surface of BTMP handsheets and allowed to dry overnight. The dried handsheets were then exposed to ambient light and dark irradiation conditions. The amount of oxidant on each handsheet was then measured as a function of time using the thioanisole test. In all cases, the injection concentration of thioanisole was 4.0×10^{-4} M.

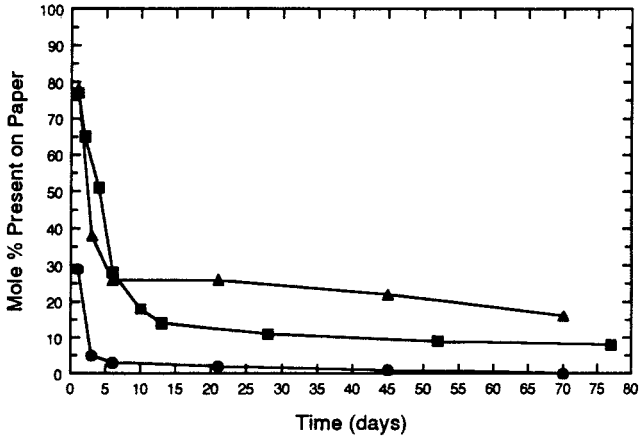

Figure 5. Mole percent of 3% sodium perborate (▲), 3% H_2O_2/3% Borax (■), and 3% H_2O_2 (●) remaining on BTMP handsheets as indicated by reaction with thioanisole.

As anticipated, BTMP impregnated with Borax alone did not exhibit any oxidative power over the 11-week test period, since Borax is not an oxidizing peroxyborate compound. BTMP impregnated with 3% hydrogen peroxide (potential injection concentration of 4.0×10^{-4} M) exhibited some oxidative power remaining on the surface early in the trial; however, this oxidative material was lost relatively rapidly (within 15 days), whereas the BTMP impregnated with a combination of 3% hydrogen peroxide with 3% Borax provided the oxidants for a much longer period of time (Figure 5). This phenomenon of oxidant retention in the pulp matrix may be due to a reaction between the Borax and hydrogen peroxide that produces in situ peroxyborate compounds that allow for better and/or longer oxidant stability, or better oxidant mobility, as suggested by Van den Berg et al.[12] McKillop and Sanderson[23] have pointed out that the presence of peroxyborate species is beneficial in nucleophilic oxidations due to their ability to deliver the perhydroxyl anion at lower pHs.

BTMP impregnated with 3% sodium perborate (potential injection concentration of 8.7×10^{-5} M) initially appeared to exhibit less oxidant remaining on the surface early in the trial, but when compared on a molar basis, the sodium perborate appeared to preserve the oxidative ability much longer than the combination of hydrogen peroxide and Borax. For example, after three weeks of exposure to ambient light, a concentration of 2.2×10^{-5} M of thioanisole was oxidized, which corresponded to over 25% of the original potential injection concentration of sodium perborate of 8.7×10^{-5} M (Figure 5). This may be due to the fact that mechanical pulps provide abundant carbohydrate structures for interactions between peroxyborate compounds and pulp fibers, as indicated by solid-state ^{11}B NMR.[11] It was suggested that reversible borate ester complexes allow for improved linkage of

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(20) Argyropoulos, D. A.; Heitner, C.; Schmidt, J. A. *Res. Chem. Intermed.* **1995**, *21*, 263−274.
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the peroxy species with the pulp, and at the same time allow the peroxyborate species to migrate freely within the pulp fiber matrix.

CONCLUSIONS

A novel method for the determination of oxidative species present within thermomechanical pulp fiber matrixes has been developed. Thioanisole (methylphenyl sulfide, MPS) is oxidized selectively and quantitatively to the corresponding sulfoxide (MPSO). By monitoring the oxidation using a normal-phase HPLC−UV system at 265 nm with diphenyl sulfone (DPSOO) as an internal standard, the developed protocol was shown to be highly reproducible, with a detection limit as low as 2.7×10^{-6} mol/L. The developed protocol could provide additional insight into the detailed mechanism of interaction of peroxy functionalities with the chromophores formed on paper during exposure to light.

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