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Effects of chemical and biological warfare remediation agents on the materials of museum objects

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ABSTRACT In the fall of 2001, anthrax-contaminated letters were sent to public figures in the United States. Chemical and radiation treatments were employed to decontaminate exposed buildings, objects, and materials. These treatments are effective, but potentially damaging to exposed objects and materials. The recommended surface chemical treatments include solutions, gels, and foams of oxidizing agents such as peroxides or chlorine bleaching agents. Such oxidizing agents are effective against a wide range of hazardous chemical and biological agents. Knowing how these reagents affect various substrates would help to anticipate and to minimize any potential damage. We are examining the effects on typical museum materials of reagents likely to be used, including hydrogen peroxide, sodium hypochlorite, and potassium peroxydisulfate. Results so far show significant changes in a number of materials. Surface corrosion was observed on metals such as copper, silver, iron, and brass. Color changes occurred with at least one reagent in about one-fourth of the dyed fabric swatches tested, and about half of the inks. Samples of aged yellowed paper are bleached. Effects varied with both the substrate and the tested reagent. The observed changes were generally less drastic than might have been expected. Enough materials were affected, though, to preclude the use of these reagents on museum objects unless no less drastic alternative is available. It appears that many objects of lesser intrinsic value can be treated without severe loss of properties or usefulness. For example, most documents should remain legible if the appropriate reagent is used. This work will provide a basis for determining which treatment is most appropriate for a specific situation and what consequences are to be expected from other treatments.

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1 Introduction

The fall of 2001 saw terrorism on a scale not previously seen in the United States. Among the problems encountered were a series of anthrax-contaminated letters sent to a number of locations including the offices of two Senators. This resulted in the contamination of the Hart Senate Office Building and its mail-handling center as well as several

mail-sorting locations. Because of the scale of contamination, gaseous fumigation with chlorine dioxide, ClO_2 , was proposed as the method of decontamination for the Senate building. However, because of the aggressive oxidizing nature of this gas, there was concern about the possible effects on artwork and sensitive technical equipment as well as personal items such as photographs in the building. Tests of exposure to a number of quickly prepared test samples showed that damage such as fading of inks, dyes, and photographs did indeed occur [1]. Mitigation of the problem by such techniques as surface treatment with oxidizing agents also was considered. In the end, the building was fumigated with chlorine dioxide after possibly sensitive or valuable objects and items were removed. These were treated separately by a number of methods appropriate to the types of objects, including chemical treatment and mechanical decontamination (HEPA vacuum cleaning). Contaminated mail, as well as later mail that would have passed through certain postal facilities, was decontaminated by electron-beam irradiation.

Chemical treatments to mitigate biohazards include the traditional agents such as hypochlorite bleaches, peroxide-based agents such as that developed at Sandia National Laboratories for chemical and biological warfare agents, and Oxone[®], a DuPont product whose active ingredient is potassium peroxydisulfate, KHSO_5 . The efficacy of each reagent depends on its concentration, method of application, and duration of exposure [2]. For non-urgent situations, the time required for decontamination is not critical. In critical situations, however, effective action may be required in a relatively short time. For example, military guidelines generally require effective decontamination within one-half hour of application. The concentrations of the active agents in decontamination formulations generally are chosen so that they are effective in such a time frame. In the test we conducted, we used standard concentrations and exposures of one-half hour in order to duplicate the types of exposure that might occur in practice. Since these are aqueous formulations, we also examined the effects of exposure to water alone in order to separate the effects of water from those of the reagents.

While these compounds and formulations can be effective in the decontamination of a range of both chemical and biological agents, all of them are potentially damaging to many of the materials of objects encountered in offices and museums. Their use may be unavoidable, however. Because there is little

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data with which to evaluate the potential damaging effects of these treatments, we initiated a study to examine their effects on various materials so that informed decisions can be made about the use of these reagents in specific situations. The same reagent may not be appropriate in all cases. For example, one reagent may be the least aggressive in corroding metals but more aggressive in altering dyes, inks, or other organic materials. If decontamination of valuable or irreplaceable objects is necessary, damage may be unavoidable but may be minimized if the appropriate information is available.

2 Experimental

2.1 Reagents and preparation of the solutions

A large variety of materials has been studied. For each material, an identical protocol was followed. Separate samples were exposed to the decontamination reagents, namely hydrogen peroxide, sodium hypochlorite (bleach), and potassium peroxydisulfate (Oxone[®]). Oxone[®] was donated by the Dupont Corporation, Wilmington, DE, USA; this is a potent chlorine-free oxidizer. Treatment in de-ionized water was also conducted to determine the effects of water alone.

All chemicals were of reagent quality and dissolved in de-ionized water at concentrations normally used for decontamination procedures. Thus, 1% Oxone[®] solutions, 3% hydrogen peroxide solutions, and 0.58% sodium hypochlorite solutions (standard 5.8% solution diluted 1 to 10) were used.

2.2 Materials

The categories of materials studied so far include metals (copper, brass, silver, tin, titanium, iron, and gold), a variety of inks from commercial pens and markers, cellulose from new and naturally aged paper samples and cotton fabrics, collagen (calfskin vellum, goat vellum, sheepskin parchment of modern manufacture, and hide glue), keratin (wool fabrics and dog hair), and fibroin (silk).

2.2.1 Metals. We treated seven metals: copper, brass, silver, tin, titanium, iron, and gold. The metals were cut into squares of about 4 sq. cm. Five samples of each were prepared, except for the gold, for which four samples of about 2 sq. cm were prepared.

2.2.2 Inks. A large number of writing inks were treated. A set of 60 inks were treated by the oxidizing reagents. Since electron-beam radiation is being used to treat mail passing through some postal facilities, more than 50 inks were also analyzed after irradiation by an electron beam (5.2 MeV at 250 μ A to a total dose of 257 kGy). Included among the inks examined were several samples of the BIC, Papermate, Pilot, and Skilcraft brands, and other pens found in the laboratory. The sample set represented a range of samples of ballpoint, fibre-tip, felt-tip, and marker pens and pencils.

2.2.3 Cellulose. Cellulosic materials of two sorts were studied: paper and cotton fabric. For the paper samples, we chose two naturally aged books, a recent newspaper, and new white paper. The older book is a German-written Bible, 'Die Bibel

oder die ganze Heilige Schrift . . .', dating from 1838. The second book is a cookbook published by Cushings and Bailey in Baltimore in 1851, 'Domestic Cookery, Useful Receipts and Hints to Young Housekeepers', by Elizabeth E. Lea. The newspaper is a sample from the Washington Post of February 10, 2002. Lastly, some white Whatman #1 paper of modern manufacture was treated. Two specimens of modern cotton textiles were treated. These were supplied by Testfabrics, Inc., and included greige cotton duck (lot 1889, style 426) and bleached cotton print cloth (lot 519, style 400).

2.2.4 Proteinaceous materials. The effects on collagenous materials were tested on four specimens obtained from our reference collection: calfskin vellum, goat vellum and sheepskin parchment of modern manufacture, and hide glue, which is from cow skins and was cast as a thin film 8 years previously.

Tests were also performed on keratinous materials. These consisted of two specimens of wool fabric, and one of dog hair. The textiles are of modern manufacture. They come from Testfabrics, Inc. The specimens of wool are ISO wool adjacent fabric (lot 2295, style 537) and 100% wool flannel (lot 662 023, style 527). The dog hair was taken from a female Siberian husky.

Specimens of silk fibroins were tested on ISO silk adjacent single fiber (lot 2299, style 615) and silk Habutae 8 mm (lot 2269, style 609).

2.3 Application

Five samples of each specimen were prepared: untreated materials were used as controls, a second sample was treated in de-ionized water, a third in the Oxone[®] solution, a fourth in the hydrogen peroxide solution, and the last in the sodium hypochlorite solution. Each sample was immersed for 30 min at room temperature, because it is the time in which a decontamination reagent is expected to be effective in a military context.

2.3.1 Metals. The samples were immersed for 30 min and then rinsed in de-ionized water. In some cases, more samples were tested and the reagents left on the samples until the solutions evaporated.

2.3.2 Inks. Ink samples were prepared by writing on Whatman paper. The first set were dried for 4 months and the second for 2 months. Each written sample was cut in five parts, immersed, and allowed to dry for a couple of days before the analyses to avoid problems of solubility [3].

A separate experiment included irradiation of inks with an electron beam (5.2 MeV at 250 μ A for a total dose of 257 kGy [3]). A double set was kept for the controls. The inks were analyzed without other treatments.

2.3.3 Cellulosic materials. Specimens of 5 cm \times 5 cm (paper) and 4 cm \times 3 cm (cotton) were prepared. After immersion the samples were allowed to dry for several days.

2.3.4 Proteinaceous materials. Samples of 2 cm \times 2 cm were cut from each material and immersed at room temperature. It

should be noticed that the hide glue was solubilized at room temperature by the sodium hypochlorite solution and by the other aqueous reagents at higher temperature. The dissolved hide-glue samples were analyzed after evaporation of the solution.

2.4 Analyses

Simple visual observation was enough to determine if a reagent had a drastic effect on a material: surface corrosion on metals, change or vanishing of colors on inks, yellowing or bleaching of cellulosic and proteinaceous materials. Effects varied with both the substrate and the tested reagent. The following analyses were performed: thin-layer chromatography (TLC) on inks, gas chromatography (GC) and attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) on cellulosic materials, and gas chromatography and high-performance liquid chromatography (HPLC) on proteinaceous materials.

2.4.1 Metals. Only visual analyses have been conducted so far, as soon as the samples were treated and six months later for the samples allowed to dry.

2.4.2 Inks. TLC was performed according to the method of Brunelle and Pro [4]; it is a visual method of separation of color components. About five plugs of ink and paper were removed and placed in a glass vial; a few drops of acetone were added to extract the ink. Sometimes a stronger solvent was necessary and pyridine was used instead of acetone. Drops of solution were spotted on silica-gel plates and the components were separated in a 1-butanol:ethanol:water (50 : 10 : 15) solvent system for 30 min.

2.4.3 Cellulosic materials. ATR-FTIR was performed on the samples of paper using a thallium iodide crystal. Paper was placed on each side of the crystal to enhance the signal.

GC was performed on samples of paper and cotton. Samples were cut into small pieces, stirred for 2 h in de-ionized water, and filtered. Sample weights varied because of the quantity available; the quantity of water was varied accordingly. Table 1 gives the weight of each sample and the amount of water used for extraction. Five ml aliquots were placed in vials and dried under vacuum for 2 to 3 days. The samples were derivatized by adding 0.1 ml of STOX reagent (25 mg/ml hydroxylamine-HCl and 6 mg/ml phenyl- β -D-glucopyranoside in pyridine) and heated for 2 h at 70 °C. Then, 0.1 ml of HMDS reagent (hexamethyldisilazane) and a drop of trifluoroacetic acid were added to silylate reactive sites. The supernatant was injected about 20 min later into a Carlo Erba HRGC 5300 series analyzer. The column was a DB-17 HT 30 m \times 0.32 mm.

Sample	Newspaper	Bible	Cookbook	Cotton
Weight	0.5 g	0.25 g	0.25 g	0.50 g
Quantity of water	25 ml	12.5 ml	12.5 ml	25 ml

TABLE 1 The weight of each cellulosic sample and the amount of water used for extraction

2.4.4 Proteinaceous materials. Amino acid analysis was performed on 1-mg samples. Each sample was placed in a 12 \times 35 mm screw-capped vial and 200 μ l of 6 N HCl then added. The vials were flushed with dry nitrogen to prevent oxidation. The samples were hydrolyzed for 24 h at 100 °C and after hydrolysis were dried under vacuum. The dried samples were then dissolved in 1 ml dilute HCl (2 ml of 12 M HCl in 1 l de-ionized water). Samples prepared in this way were analyzed directly on a high-performance liquid chromatograph (HPLC) especially designed for ion-exchange separation of amino acids. Analysis was performed on a St. John model 2000 amino acid analyzer using an Alcott 708AL autosampler. This technique allows for the separation and quantification of most of the amino acids found in proteinaceous materials; however, it does not detect secondary amines such as the two common imino acids proline and hydroxyproline [5].

For gas chromatographic analysis, 150 μ l aliquots from the 1 mg/ml solution were taken and dried under vacuum using a liquid-nitrogen trap. The dried samples were derivatized with trifluoroacetic anhydride (TFAA) and thionyl chloride. Analysis was conducted on a Hewlett Packard 6890 series gas chromatograph using a nitrogen-phosphorus detector. The column was a Chirasil-Val 25 m \times 0.25 mm that enables the separation of D-amino acids from their L-amino acid counterparts.

2.5 Results

2.5.1 Metals. A visual observation allowed us to see some corrosion on certain metals, while some of them were not affected at all. Thus Oxone[®], hydrogen peroxide, and sodium hypochlorite had no effect on tin, titanium, and gold. Degradation by Oxone[®] on the copper, brass, silver, and iron samples was readily apparent. Hydrogen peroxide affected only the copper and sodium hypochlorite affected the silver and the iron. Table 2 summarizes the observations. Six months after the treatment the corrosion has increased on the samples on which sodium hypochlorite was allowed to dry.

2.5.2 Inks. A large number of inks have been analyzed by TLC. For the treatment by electron irradiation, we compared the sample not irradiated with the sample irradiated. For each ink treated chemically, we compared visually the spots of the control sample and the samples immersed in water, Oxone[®], hydrogen peroxide, and sodium hypochlorite.

- Electron irradiation. More than 50 inks were irradiated. Visual observation did not show any change in the ink colors, only the paper turned yellow. 46 inks could be dissolved in acetone or pyridine and 11 of the 46 inks showed changes on TLC analyses. For most of the inks, these changes consisted of the presence of a new component. The results for altered inks are summarized in Table 3.
- Chemical treatment. Immersion in water and hydrogen peroxide left the inks unchanged or slightly diminished in intensity. The use of immersion in water alone as a control allows an evaluation of the effects of the addition of oxidizing reagents. About one-third of the inks treated with Oxone[®] showed obvious differences: the color faded, disappeared, or changed. Sodium hypochlorite is the most aggressive reagent: all the inks were affected, except Crayola

	Water	Oxone® – 30 min	Oxone® – dryness	H ₂ O ₂ – 30 min	H ₂ O ₂ – dryness	NaOCl – 30 min	NaOCl – dryness
Copper	No Change	Change of color (orange, purple) and corrosion: oxone is very oxidizing	N/A	Change of color (orange)		No change	Change where the drops have dried, the sample has become almost entirely yellow after six months
Brass	No Change	Degradation: oxone is very oxidizing	N/A	No change	No change	No change	Irregular corrosion where the drops have dried (become pink after six months)
Silver	No Change	Degradation: oxone is very oxidizing	N/A	No change	No change	Very degraded	N/A
Tin	No Change	No change	No change	No change	No change	No change	No change
Titanium	No Change	No change	No change	No change	No change	No change	No change
Iron	No Change	Very degraded: oxone is very oxidizing	N/A	No change	No change	Rust on the edges (worse after six months)	N/A
Gold	No Change	No change	No change	No change	No change	No change	No change

TABLE 2 Visual changes in the metal samples exposed to decontamination reagents

Name of sample	Color	Change
Skilcraft US gov. fine	Blue	New blue component
Skilcraft felt tip	Blue	New blue component
Skilcraft marker	Blue	New pink component
Skilcraft marker	Red	New red component
Papermate med. pt.	Blue	New blue component
Bic round Stic med.	Blue	New blue component
Schwan Stabilo	Red	Altered mobility of component
Skilcraft US gov. USA	Blue	New blue component
Vista by Skilcraft fine	Black	New yellow component
Skilcraft US gov. med.	Blue	New blue component
BIC wide body Mexico	Black	One purple component disappears and a new one appears

TABLE 3 Changes in inks altered by electron-beam irradiation

green and Berol blue. The color disappeared in one-third of the cases and faded in the other cases.

A certain number of inks totally disappeared because of their solubility during the immersion; this was the case with Papermate metal roller micro blue, Skilcraft highlighter blue, Avery Dennison Hi-Liter blue, Skilcraft highlighter green, Skilcraft felt blue, Skilcraft felt green, Skilcraft felt black, Schwan Stable red, and Papermate metal roller micro red. Some inks could not be dissolved in any solvent, so about 40 inks were analyzed. More than half of the inks were affected by Oxone® or sodium hypochlorite. The changes observed are usually the appearance or the disappearance of one component. With the red inks, one or two new components always appeared after immersion in NaOCl, while with the black and blue inks one component generally disappeared.

2.5.3 Cellulose. The treatments by Oxone®, hydrogen peroxide, and sodium hypochlorite did not affect the appearance of the samples of cotton, but we could see some changes on samples of paper. The newspaper yellowed when treated by Oxone® and sodium hypochlorite while the 1838 Bible

and the 1851 cookbook papers were bleached. Hydrogen peroxide had few apparent effects on the specimens of paper.

- Cotton. The analyses by gas chromatography did not show any differences between the five samples of cotton duck and the five samples of bleached cotton. Apparently little material was leached or altered during the hydrolysis.
- Paper. The two important degradation components of paper are glucose and xylose. In all cases the quantities of glucose and xylose were smaller after treatment by water, hydrogen peroxide, and sodium hypochlorite, but equivalent between samples. The opposite occurred with Oxone®, particularly with the newspaper in which a large peak of xylose appeared. The wood-pulp newspaper includes significant amounts of xylan, which is easily degraded to yield xylose (see Figs. 1 and 2). These effects are less pronounced in the samples of the 1838 Bible and the 1851 cookbook (see Figs. 3 and 4). Some tests were conducted on newspaper with a 5% Oxone® solution instead of a 1% Oxone® solution and with a longer exposure time with the 5% Oxone® solution. More xylose is released

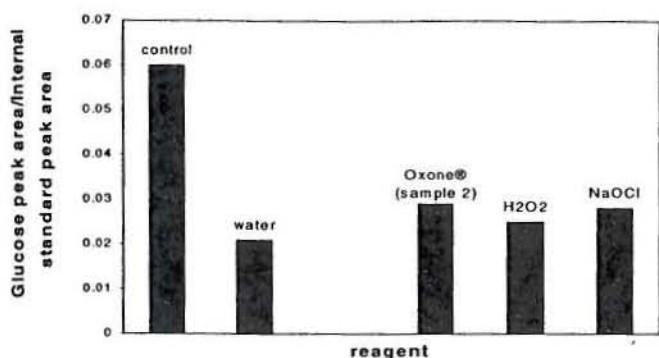


FIGURE 1 The relative glucose concentration in treated and untreated newspaper samples

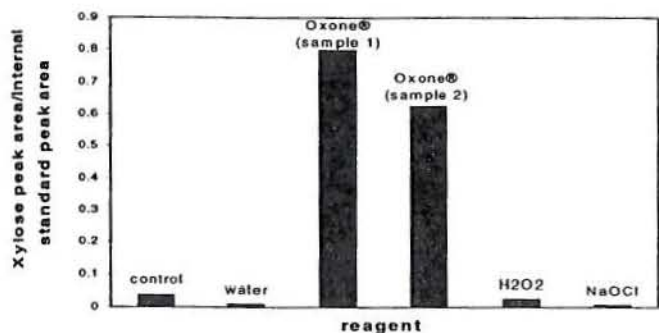


FIGURE 2 The relative xylose concentration in treated and untreated newspaper samples

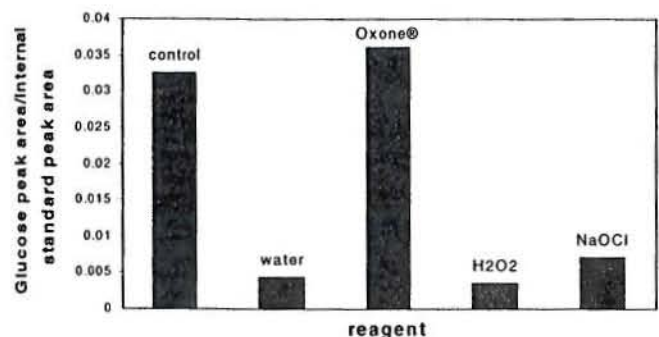


FIGURE 3 The relative glucose concentration in treated and untreated cookbook samples

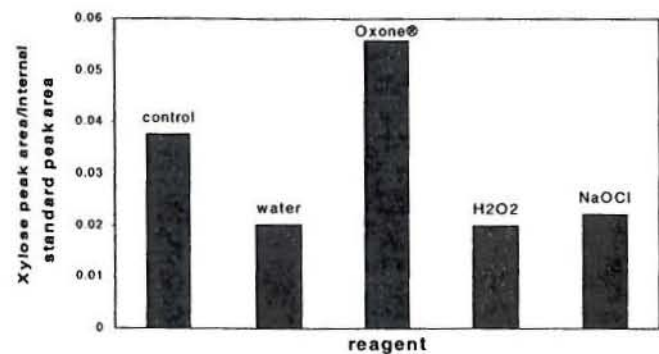


FIGURE 4 The relative xylose concentration in treated and untreated cookbook samples

with the 5% Oxone® solution than with a 1% solution (see Fig. 5), but the exposure time has no effect (see Fig. 6).

On Whatman paper no significant differences were seen.

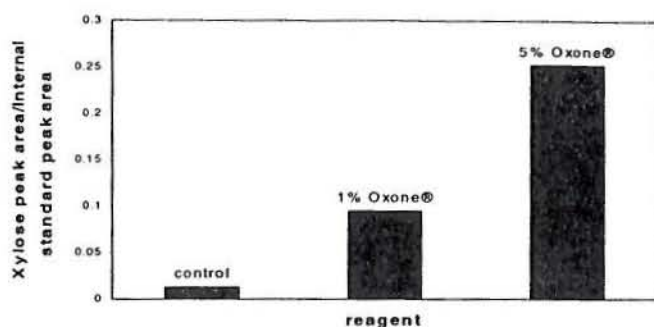


FIGURE 5 The relative xylose concentration in untreated newspaper samples, and samples treated with 1% Oxone® and 5% Oxone®

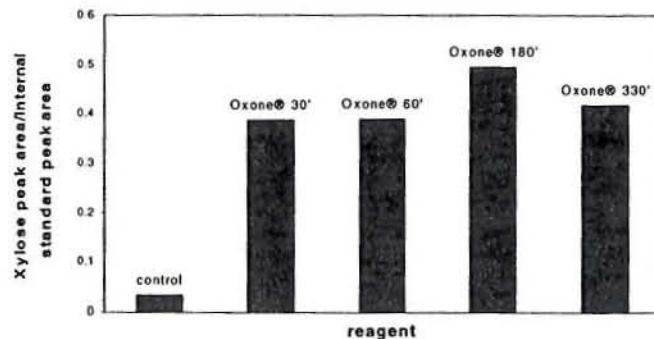


FIGURE 6 The relative concentration of xylose in newspaper samples as a function of time of exposure to a 5% Oxone® solution

The ATR analyses did not show any significant differences. Most of the time, the spectra were essentially identical and were superimposable. There were no new peaks. The profiles of some Oxone® samples were slightly different, but this may be due to the difficulty of reproducing IR spectra of surface samples.

2.5.4 Proteinaceous materials.

- Collagen. Most of the time, we noticed a change of color on the samples of goat vellum, calfskin vellum, sheepskin parchment, and hide glue. Generally the treatments yellowed the samples. They bleached them in only two cases (sheepskin parchment treated by Oxone® and hydrogen peroxide).

Treatments were evaluated by comparing the amino acid profile of samples after treatment with that of the untreated specimen [6]. The purpose was to evaluate any changes in the amino acid composition, which is generally accompanied by an increase in ammonium ion (NH_4^+). Most of the time, some slight reductions in the valine, isoleucine, and leucine values were observed, possibly as an artifact of the preparation of the sample, and a decrease in the concentration of ammonium ion. During the 30-min immersion this ion is probably washed out. For instance, the sheepskin parchment specimen did not show any significant change; the distribution of the amino acids in water is similar to that of the treatments by Oxone® and NaOCl. Figure 7 shows the results of the sheepskin parchment treated with Oxone®; the plot shows the before and after treatment concentrations in parts per thousand of each of the amino acids measured. The most dramatic change seen was with the treatment by hydrogen peroxide (see Fig. 8). Even at

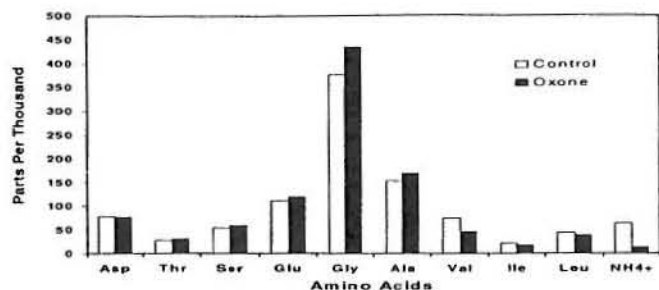


FIGURE 7 The amino acid profile for sheepskin parchment before and after immersion for 30 min in a 1% Oxone[®] solution. The amounts are reported as a fraction of the total amount of the listed amino acids detected

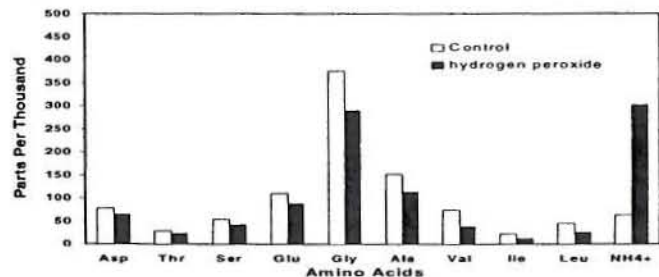


FIGURE 8 The amino acid profile for sheepskin parchment before and after immersion for 30 min in a 3% hydrogen peroxide solution. The amounts are reported as a fraction of the total amount of the listed amino acids detected

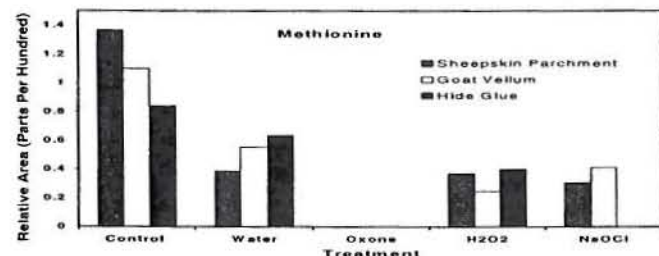


FIGURE 9 The changes in methionine content of treated and untreated samples of sheepskin parchment, goat vellum, and hide glue. The amounts are reported as a percent of all material detected. Note the complete loss of methionine in all peroxymonosulfate treatments

3% concentration this reagent can alter the amino acid profile of the protein. All of the amino acids are reduced and the amount of NH_4^+ decomposition product is greatly enhanced. Figure 9 shows the reduction of the sulfur-containing amino acid, methionine, for the sheepskin parchment, goat vellum, and calf vellum after each of the treatments. While this amino acid is present only in small amounts, it is interesting that it essentially completely disappears after treatment with Oxone[®]. Because methionine is oxidized relatively easily, one might expect all of the tested reagents to lower the concentration of methionine. The differences seen may be due more to steric effects than to differences in the potential power of the reagents. For example, hypochlorite reduces the concentration of methionine in the insoluble parchment and vellum, but is able to remove all of the methionine only in the hide glue, which dissolves during the treatment.

– Keratin and fibroin. A visual observation of the samples after immersion indicated some changes of color. The

samples of silk and wool treated by Oxone[®] and NaOCl yellowed, slightly with Oxone[®] and drastically with NaOCl. The samples of wool treated by H_2O_2 bleached. The silk is already white, and no apparent differences were observed. The dog hair is drastically affected by NaOCl only: the reagent stuck on the hair and yellowed it. We are currently conducting amino acid analysis; the results will be available in a forthcoming publication.

3 Discussion and conclusions

The results presented here demonstrate quite clearly that these reagents can cause damage to the types of materials found in museum objects. However, the degree of damage, if any, varies with both the reagent and the substrate to which it is applied. Thus damage can be minimized with the appropriate choice of treatment. For example, of the reagents tested, hydrogen peroxide is generally the least aggressive reagent for the treatment of metals, but sodium hypochlorite may be preferred for the treatment of copper objects if it can be rinsed off effectively. Oxone[®] seems to be the most aggressive in attacking organic materials such as cellulose and collagen, but sodium hypochlorite affected a much higher percentage of inks. In some cases, a decision may depend on whether the types of material present can be readily and reliably identified. If possible, any decision relating to the treatment of a collection should be made by or after discussion with someone who is familiar with the collection. Evaluations of the types of treatments that would be most appropriate can be made when surveys of collections are conducted.

It is unfortunate that planning for contingencies such as chemical or biological contamination must be included as a consideration in the management of collections. In emergencies, the preservation of human life must take priority. There may be little or no time to consider the preservation of objects. Information that can reduce the possible damage to objects without reducing the efficacy of decontamination treatments should be available and be provided quickly.

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