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# An investigation into the deacidification of paper by ethoxymagnesium ethylcarbonate

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Aspects of the procedure used since 1995 by the British Library whereby paper is deacidified with ethoxymagnesium ethylcarbonate (EMEC) in hexamethyldisiloxane (HMDS) have been studied using scanning electron microscopy (SEM) along with energy dispersive X-ray analysis (EDAX), X-ray fluorescence (XRF) spectrometry and particle-induced X-ray emission (PIXE). The treatment was applied to three types of test paper, and the analytical results compared with those for similar samples treated using a method which mimicked as closely as possible the library's previous deacidification procedure; this involved the use of the now-banned solvent trichlorofluoroethane. The amount of EMEC distributed over the whole paper sample was fairly consistent for each paper type, but microscopically it was found to be congealed into large deposits, possibly hydrolysed by moisture in the paper, and not distributed as evenly among the paper fibres as is either desirable or possible. The depth of penetration of the EMEC particles obtained by spraying only one side of the paper is found to be poor for paper of heavy gauge and high moisture content, the thinnest samples retaining little alkaline buffer. The results obtained by the newer procedure were similar to those obtained by the older one, and no HMDS either reacted with, or remained in, the paper despite the relatively long drying time.

The principal cause of the deterioration of cellulose-containing materials, especially paper, was identified in the 1950s to be sulfuric acid generated by the hydrolysis of the common sizing agent aluminium sulfate[1] (referred to, somewhat misleadingly, as 'paper makers' alum'). Aluminium sulfate is used in conjunction with natural wood resins to control water penetration in paper. Traditionally it was used to deposit saponified resins onto the surface of paper fibres during manufacture so as to achieve the desired firmness and to prevent the blurring of dyes and inks.[2] Other causes of acidity include the oxidation of lignin and cellulose and the absorption of atmospheric pollutants;[3] indeed, any acidic environment, regardless of the source of the acidity, affects paper in the same way, initiating ageing processes that affect the lengths of the cellulose chains, resulting in brittleness and fragility.[2] The library and museum community are obliged to preserve printed matter that was prepared on poor-quality (acidic), mass-produced paper; such items, for example newspapers or the scribbled first drafts of now famous manuscripts, were often intended to be ephemeral but now have a high cultural value. The deacidification of these items to preserve them for future generations is a major concern of librarians and archivists world-wide.[2–17] However, the mass deacidification of paper is also controversial. The current method of evaluating the 'pH of paper' is known to be flawed, as it is really the pH of the solution used to moisten the paper surface that is being measured by a conventional pH probe; there is thus the real possibility that millions of folios are being treated needlessly because they are being deemed, incorrectly, to be too acidic. This controversy will continue until a method is devised to measure the pH of moisture trapped inside the actual paper fibres, thereby yielding the true 'pH of the paper'.[18,19]

The research reported here is an investigation into the effectiveness of the delivery procedure of the mass deacidification agent EMEC used in the British Library (BL). Many treated and untreated samples have been examined by X-ray fluorescence (XRF) spectrometry, scanning electron microscopy (SEM) and associated energy dispersive X-ray analysis (EDAX), and particle-induced X-ray emission (PIXE) to establish the uniformity of distribution and depth of penetration of the deacidification agent EMEC among paper fibres.

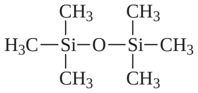
Due to the large number of documents to be treated in the BL, a deacidification solution must be priced reasonably and, moreover, it must also penetrate each book uniformly in a moderate period of time, and provide a sufficient alkaline reserve for prolonged performance.[10] Over the past two decades, the trend has been towards using non-aqueous solvents to deliver the deacidification agent, some of which involved CFC chemicals that have now been phased out due to environmental legislation. In 1995, the BL changed their delivery solvent from trichlorofluoroethane to polydimethylsiloxane, but the latter was found to be slow to dry causing inks to be fugitive and even tide-mark stains to develop.

The new paper preservation technique is based upon ethoxymagnesium ethylcarbonate (EMEC, **1**), which is the deacidification agent, and the siloxane solvent, hexamethyldisiloxane (HMDS, **2**).[20]

The EMEC reacts with the acid in the paper (in this example, sulfuric acid) in a similar way to that discussed for other organometallic deacidification agents [Scheme 2(a)].[21] MgO formed from the primary hydrolysis product [Scheme 2(b)][21] reacts with $CO_2$ to form the desired buffer, $MgCO_3$. The source of the $CO_2$ may be the hydrolysis of the ethylcarbonate ligand, but comparison with the similar Batelle

$C_2H_5OCO_2MgOC_2H_5$

**1**



$$H_3C-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3$$

**2**

**Scheme 1** Ethoxymagnesium ethylcarbonate (EMEC, **1**) and hexamethyldisiloxane (HMDS, **2**).

process[2] (*vide infra*) suggests that it is probably atmospheric.

$$C_2H_5OCO_2MgOC_2H_5 + H_2SO_4 \rightarrow MgSO_4 + CO_2 + 2C_2H_5OH \quad \text{(a)}$$

$$C_2H_5OCO_2MgOC_2H_5 + H_2O \rightarrow MgO + CO_2 + 2C_2H_5OH$$
$$MgO + CO_2 \rightarrow MgCO_3 \quad \text{(b)}$$

**Scheme 2** (a) An example of EMEC deacidification and (b) a proposed mechanism for the formation of the desired buffer.[21]

There are three questions of interest: first, whether the HMDS solvent permits a more uniform distribution of the EMEC than does the CFC solvent; second, whether the HMDS detaches from the cellulose fibres after application; and third, whether the depth of penetration of the EMEC particles could be determined (the solution is normally applied to one side of the paper only, and thus the EMEC particles may not penetrate through to the other side before the solvent evaporates). Hereinafter, all Mg-containing particles related to EMEC will be described as EMEC particles; this is used as a generic term and no distinction is made as to whether the compound has reacted with acid, been hydrolysed, or perhaps not reacted, as only the presence of a magnesium-containing compound is determinable.

The deacidification agent and the bulk solvent both contain the elements Mg and Si not associated normally with organic materials such as the cellulose fibres of paper, although they are associated with sizes, loads and impurities, and therefore control samples were used extensively. Elemental analysis targeting these two elements in particular was considered to be the most perceptive approach to this project, *via* XRF spectrometry, SEM, EDAX analysis and PIXE techniques.

## Experimental

### Preparation of paper samples

Three different types of paper studied: 20th century newsprint (mechanical wood fibres, 50–60 g m$^{-2}$, 6–9% moisture content, calliper 0.08 mm); general 1920s print (chemical/mechanical wood fibres, 80–90 g m$^{-2}$, $\leqslant$5% moisture content, calliper 0.13–0.14 mm); and 18th century handmade (rag linen fibres, 100–120 g m$^{-2}$, 5–8% moisture content, calliper 0.20–0.25 mm). The BL provided over 70 paper samples (9 cm × 9 cm), including untreated controls, 27 samples treated with EMEC in HMDS, and 27 samples treated with EMEC in the solvent 1,1-dichloro-2,2,2-trifluoroethane (DCTFE). As it is now impossible to obtain CFC solvents in the UK, DCTFE, which itself will be banned early next century, was substituted for trichlorofluoroethane. The samples were treated in-house by the BL following their usual deacidification procedure. They were cut to size and then placed on a wire-mesh treatment screen and held in place by a suction motor (air velocity *ca.* 1.4 m s$^{-1}$). The freshly prepared deacidification solution, propelled by nitrogen at a pressure of 3.85 kg cm$^{-2}$, was sprayed by hand from approximately 10 cm in a sweeping motion until 'full saturation' was achieved.[22]

Sixteen 2 cm × 2 cm sub-samples were removed from each of 33 of the 9 cm × 9 cm samples, including 6 controls, and the positions of the sub-samples in the original samples were recorded. Four 40 mm circular sub-samples were removed from each of the remaining treated samples and six controls to take advantage of the optimum sampling area (XRF spectrometry); the original positions of the sub-samples were again recorded. In total there were 660 samples available for analysis, representing equally each paper type and each delivery solvent, and with sufficient standard samples.

### Scanning electron microscopy and energy dispersive X-ray analysis

A study of 66 samples and 12 standards was performed on a JEOL JSM-6400 scanning electron microscope with an accelerating voltage of 5 kV and an EDAX attachment. The samples were mounted on 40 mm aluminium discs and sputter-coated with a 5–10 nm film of gold and palladium.

### X-Ray fluorescence spectrometry

48 samples and 12 standards were analysed by XRF spectrometry using a Philips PW 1480 sequential X-ray spectrophotometer. The radiation source was a rhodium lamp with wide-band excitation operating at 60 kV and 40 mA. The crystals used were InSb (Si analysis) and thallium azide phthalate (Mg analysis) and the number of counts was measured by a flow counter. Both sides of the samples were studied and, for each, six recordings and background counts (collection time = 40 s) were performed for the Mg analysis, and four recordings and background counts (collection time = 16 s) were performed for the Si analysis.

### Particle-induced X-ray emission

Elemental depth profiling was carried out by detecting X-rays generated as a result of scanning a focused beam of 3.0 MeV protons over the cross-sections of the paper samples. The results produced in the form of maps and line-scan plots were obtained using the scanning proton microprobe facility at the University of Oxford. The experiments were performed using a 1 μm wide proton beam spot, and the X-rays produced were detected using a conventional Si(Li) detector. Further details about the experimental arrangements and new developments in the application of ion-beam analysis (IBA) to historical materials (including paper) are presented elsewhere.[23,24] A novel experimental procedure was developed for this study and will be published subsequently.

## Results and discussion

### Scanning electron microscopy and energy dispersive X-ray analysis

At a relatively high magnification (× 6000) it was possible among the paper fibres to detect white particles, which were rarely greater than 1 μm in diameter and often much smaller: an example of the type of image observed is shown in Fig. 1(a). The particles were almost spherical and analysis using EDAX revealed that they contained magnesium. The particles were small and of regular shape and their presence in all of the EMEC samples treated, their magnesium content, and the lack of any other element with a relative atomic mass $>$23, proves that they are derived from the EMEC deacidification agent.

Other particles were found amongst the paper fibres but, due to their shape, size and analysis by EDAX, they could not be confused with the EMEC particles. The results of the EDAX analysis are listed in Table 1.

Apart from the EMEC, the most important particles to be identified in the general and newsprint samples were irregular crystals with both a high Al and, importantly, high Si content; they are probably an aluminosilicate clay. The high Si content of these particles will have an important bearing on the interpretation of the results of the PIXE and XRF spectrometric analysis (*vide infra*).

In the test samples examined, there were generally significantly more EMEC particles on the sprayed side than on the unsprayed side. An extreme example is illustrated in Fig. 1(a) and (b): one side of a general print/HMDS sample [the sprayed side, Fig. 1(a)] was well covered in what was, for this study, a well above average number of EMEC particles, but on the reverse [unsprayed side, Fig. 1(b)] such particles are

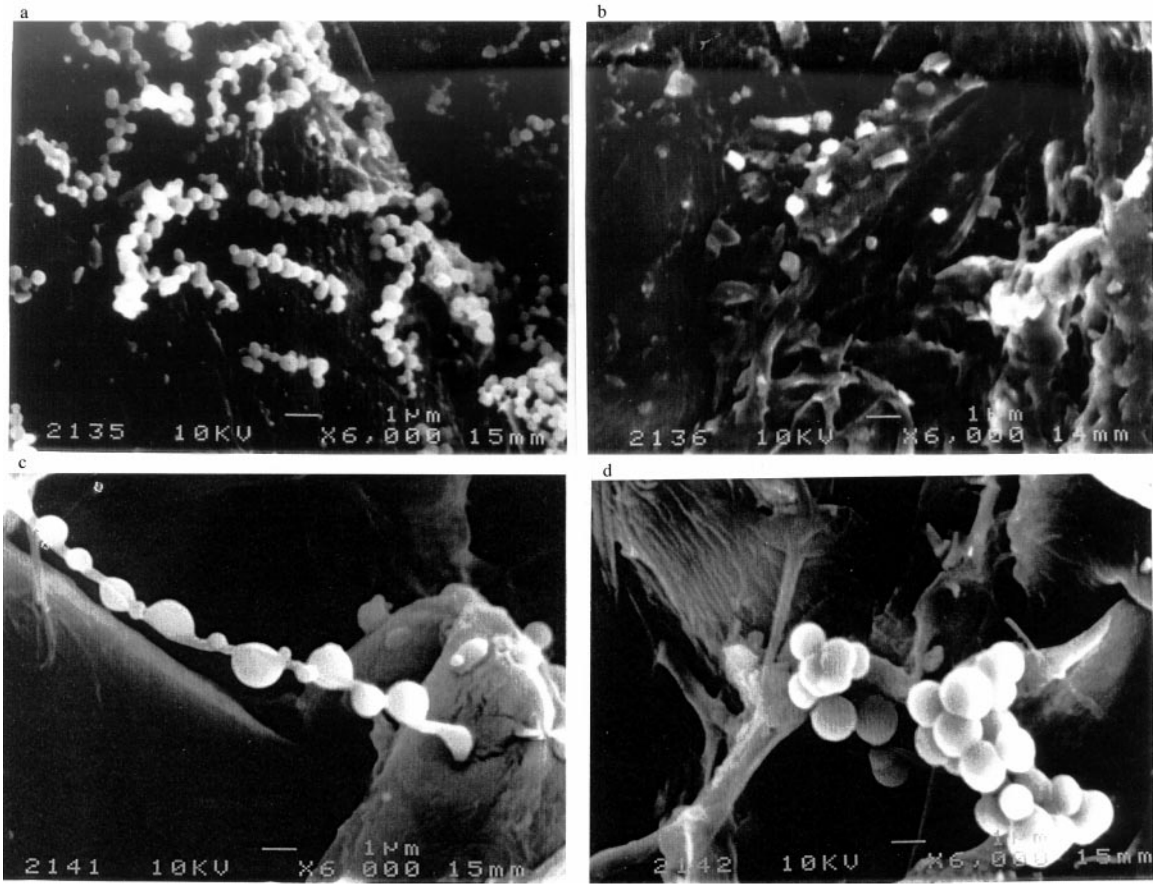


**Fig. 1** Electron micrographs of (a) EMEC particles on a general print samples ×6000, (b) EMEC particles on the reverse of general print samples in (a) ×6000, (c) 'strings' of EMEC particles ×6000, (d) 'bunches' of EMEC particles ×6000.

represented, but on a much lesser scale. This was generally true for all of the samples examined, regardless of whether the deacidification agent was delivered in the DCTFE or siloxane solvent.

Using SEM/EDAX it is not possible to judge the depth of penetration of the particles but only possible to examine each side of a sample to see whether EMEC particles are represented. By this method, the following conclusions could be made as to the effectiveness of the penetration of the particles for the different paper types: (1) some EMEC particles were always observed on both sides of the newsprint samples, but for the thicker handmade paper very few if any penetrated to the reverse side. Newsprint paper is thin, and this is the likely reason for the better penetration; (2) in the case of the general print samples, EMEC particles were always observed on both sides, but Fig. 1(a) and (b) indicate the relative ineffectiveness of the penetration to the reverse. Furthermore, the presence of ink on the sprayed side of the samples blocks the penetration of the deacidification agent.

Generally, therefore, the depth of penetration achieved by spraying on one side of the paper depends only upon the thickness of the paper and whether or not there is ink on the sprayed side. However, even where one side of the thinnest paper is well covered in EMEC particles, there are many fewer EMEC particles on the reverse.

The conclusions drawn above are dependent in a large way on how many particles were deposited on the sprayed side of the paper samples in the first place. The type of coverage illustrated in Fig. 1(a), for which the sample had been sprayed with the siloxane-based solvent, was greater than that of any other sample examined, and in most cases it was much greater. More representative examples are shown in Fig. 1(c) and (d), which show isolated groups of EMEC particles in paper samples treated with the siloxane solvent. Generally, for all paper types and both solvent delivery systems, these groups of particles were few and far between.

Two significant observations can be made from the images observed in this experiment: (1) even on the samples (those with the sides sprayed) with the most EMEC particles, the distribution is very uneven for all of the paper types, with isolated groups of particles dotted around the samples; (2) the particle size is generally larger on all of the newsprint, handmade samples and the general print samples examined which had been treated with the DCTFE-based agent, than it is for the general print samples treated with the HMDS-based solution [Fig. 1(a)–(d) are all at the same magnification, ×6000].

**Table 1** EDAX analysis of crystals found between the paper fibres

| Elements identified (relative atomic mass $<23$) | Identity of compound | Paper type[a] and notes |
|---|---|---|
| Mg | EMEC or magnesium salt product | Treated G, H & N |
| Ca and S | Gypsum,$CaSO_4 \cdot 2H_2O$ | G and H. Probably added as a load |
| Ca | Chalk, $CaCO_3$ | G |
| Fe, K and S | Alum, $AlK(SO_4)_2 \cdot 12H_2O$ | G. Probably added as a size |
| Al and Si | Aluminosilicate clay | G & N. Probably added as a load |

[a] G = 1920s general print, H = 18th century handmade and N = 20th century newsprint.

It was common for the EMEC particles to form either 'strings' [Fig. 1(c)] or 'bunches' [Fig. 1(d)] on the samples that displayed larger EMEC particles (the 'string' between the particles in Fig. 1(c) is formed by the EMEC). The smaller particles in some general print examples treated with the HMDS-based solution do also coagulate, but they tend to distribute much more widely.

The particles on most of the paper samples examined are up to ten times the diameter of the smallest observed on the general print samples treated with the siloxane-based solution. The smaller particles obviously give better coverage where they are deposited, although they can still be spread inconsistently across the general print samples treated with the HMDS. The large particle size and 'bunching' of the EMEC particles on all of the other sample types reinforces the poor distribution of the deacidification agent. A possible cause is that the EMEC/HMDS solution is very water sensitive, and a white product, $MgCO_3$, drops out of solution if the deacidification solution is contaminated with moisture.[22] A similar problem was noticed in the development of the Battelle process, employed by the Deutsche Bibliothek,[2] which uses the same solvent as the BL but a different deacidification agent, $Mg(OC_2H_5)_2$. This alkoxide also hydrolyses to the desired buffer, $MgCO_3$, but this can occur rapidly in humid conditions, affecting the uniformity of distribution.[2] The Battelle process therefore includes a pre-drying of the samples from their stored humidity of 5–7% by weight to a water content of less than 1%.[2]

The BL do not pre-dry their samples, and this may be the reason for the clumping of particles observed generally in the handmade and newsprint samples, both of which have a relatively high moisture content. The general print samples, however, have the lowest moisture levels, as is expected for mechanical papers of such an age with degraded cellulose fibres. It is possible that the good spread of EMEC particles in some of the general print samples examined is attributable to a lack of moisture, implying that pre-drying will assist the distribution and so the effectiveness of the deacidification agent. It seems that the distribution of the EMEC particles among the paper fibres is typically less efficient than is either desirable or achievable.

### X-Ray fluorescence spectrometry

The mean of the number of counts (minus the background count) for Si and Mg was calculated and a standard deviation obtained for each sample. The normality of distribution of the number of counts for each sample set was established for both the Mg and Si analysis ($3\sigma$ error test). However, the mean number of counts between similar samples (*e.g.* the unsprayed sides of EMEC/HMDS general print samples) were always found to differ significantly using the statistical technique of analysis of variance (ANOVA, $P=0.05$) whereby the variance of each element within the same sample group and between similarly treated samples is compared. In other words, the amount of Mg and Si detected in samples treated identically varies significantly.

As the number of counts is relative for each sample, it is possible to determine the range of the relative amounts of each element detected on samples treated in an identical way (Table 2). Though there is no statistical similarity between the relative amounts of each element detected on similar samples, the tabulated data convey important information regarding the distribution of each element in the paper samples. Thus the amount of Mg present in the standard (untreated) samples is consistently low for each type of paper, and probably results from impurities that entered the paper during manufacture, rather than from substances added deliberately. By contrast, the level of Si detected in the standard samples varies considerably for the three paper types. The level of Si detected on the general print standards is about three times more than on the newsprint standards, and over 40 times that detected on the handmade samples. From the EDAX analysis, it is known that aluminosilicate clays are present in significant quantities in the general print samples, and to a lesser degree in the newsprint samples: they are probably added deliberately to fill the paper, and are the source of the high Si content. The very low relative amounts of Si on the handmade paper indicates that little or no Si-containing compounds were added deliberately at manufacture.

Higher levels of Mg were detected on all of the treated paper samples relative to the standard samples. For the general print samples, there was a higher level of Mg on the sprayed side, but considerable amounts were detected on the unsprayed sides as well. There was little difference between the average amounts of Mg detected whether the EMEC was delivered in the HMDS or DCTFE. The range of the relative amounts of Mg detected does suggest that the EMEC/HMDS has slightly better penetration, which would be explained by the smaller particle size.

For the handmade samples, there was a vast difference between the amount of Mg detected on the sprayed and unsprayed sides. On average, more Mg was detected on the sprayed sides of the samples treated with EMEC/DCTFE than those sprayed with EMEC/HMDS. The most important observation, however, is that the amount of Mg detected on the reverse of the handmade samples was very low, comparable to that on untreated samples. In agreement with the SEM observations, this suggests that very little EMEC penetrates the thick-gauged handmade paper, regardless of the carrying solvent. The relatively high moisture content of the handmade paper may also contribute to this observation due to the EMEC particles being hydrolysed before they can penetrate deeply into the paper.

The most surprising observation was the relatively low levels of Mg detected on the treated newsprint samples. The amounts were higher than detected on the untreated standards, but not by as much as had been expected. Similar amounts of Mg were detected on the sprayed and unsprayed sides, suggesting that the thin gauge of the paper aided the even distribution of the particles; but, as the samples of the three papers were treated identically, the thin gauge of the newsprint does seem to inhibit its potential to retain a sufficient alkaline reserve before becoming saturated.

Both sides of four circular sub-samples, 40 mm diameter, were examined for each 9 cm × 9 cm original. The samples covered 62% of the whole area of each sprayed sheet. Strikingly variable relative amounts of Mg were sometimes found in sub-samples from the same original (*e.g.* a ratio of 0.42 : 0.51 : 0.83 : 1.0 on four different samples from the sprayed side of one general print/HMDS sample), but the relatively low readings in this sample were extreme. The variations tended to be greater between original samples than within the same sample. Overall, the least amount of Mg detected was rarely less than half the maximum amount detected on similar sub-samples, and this suggests that the spraying technique with either solvent is depositing the EMEC fairly evenly on a macro-scale; but as the SEM analysis revealed, the distribution on a micro-scale within the paper fibres is poor.

Hexamethyldisiloxane has a relatively low boiling point (100 °C), a relatively high vapour pressure (20 mbar at 20 °C) and a low enthalpy of vaporization ($186\ \mathrm{kJ\ kg^{-1}}$), which means that treated papers will dry fairly quickly. However, this solvent dries much more slowly than the trichlorofluoroethane used previously, giving rise to concern that the prolonged exposure of the paper to the siloxane solvent may have adverse effects and that the solvent may even react with species within the paper or the paper fibres themselves, depositing unknown silicon-containing compounds within the paper.

The results of the XRF analysis displayed in Table 1 suggest

**Table 2** Range and weighted mean of relative number of counts determined from similar samples for Si and Mg by XRF spectrometry

| Paper type | Deacidification solution solvent | Sprayed (S) or unsprayed (U) side | Range of relative number of counts and weighted mean (in parentheses) Si | Mg |
|---|---|---|---|---|
| General print | HMDS | U | 21.5–32.9 (28.7) | 0.17–0.36 (0.26) |
| | | S | 29.7–44.5 (37.6) | 0.19–0.49 (0.39) |
| | DCTFE | U | 22.1–30.6 (28.1) | 0.16–0.28 (0.24) |
| | | S | 21.9–40.3 (33.3) | 0.32–0.46 (0.41) |
| | Standard | | 28.4–31.9 (29.9) | 0.06–0.09 (0.08) |
| Handmade | HMDS | U | 0.45–0.59 (0.49) | 0.02–0.04 (0.03) |
| | | S | 0.41–0.82 (0.54) | 0.14–0.20 (0.17) |
| | DCTFE | U | 0.31–0.42 (0.37) | 0.08–0.09 (0.09) |
| | | S | 0.50–0.67 (0.60) | 0.42–0.55 (0.48) |
| | Standard | | 0.67–0.80 (0.71) | 0.07–0.09 (0.08) |
| Newsprint | HMDS | U | 8.63–12.66 (10.1) | 0.06–0.08 (0.07) |
| | | S | 8.60–12.71 (10.1) | 0.06–0.08 (0.07) |
| | DCTFE | U | 8.01–10.97 (9.71) | 0.06–0.09 (0.08) |
| | | S | 8.21–11.52 (9.53) | 0.07–0.10 (0.08) |
| | Standard | | 10.1–12.42 (11.2) | 0.02–0.04 (0.03) |

that the HMDS solvent is not retained by the treated paper. There is no significant difference between the ranges of the amounts of Si detected, regardless of whether the paper types were standard samples, or ones treated with either the siloxane-based or the DCTFE solution. This is particularly apparent in the handmade samples, which already contain a relatively low amount of Si, and where those samples treated with EMEC/HMDS actually contained the lowest average amount of Si.

### Particle-induced X-ray emission spectrometry

The similar profiles of the line-scan plots obtained for Al and Si from general print and newsprint samples treated with EMEC/HMDS [*e.g.* Fig. 2(a) and (b)] confirm that they predominantly co-exist, which corresponds to the observation by SEM/EDAX that aluminosilicate clays are present. This supports the observation that Si present on the paper samples is due neither to the HMDS solvent nor to any reaction products, but to additives or impurities in the manufacturing process. The similar profiles of the plots obtained for Ca and S [*e.g.* Fig. 2(c) and (d)] from the handmade and general print also confirm that these elements co-exist as gypsum.

The depth profile of the distribution of Mg, as illustrated by line-scan spectra, show that the maximum concentration of Mg is at a depth of roughly 50–70 μm (*i.e.* about one-third to one-half the way through) into the paper for the general print samples [*e.g.* Fig. 2(e) and (f)]. This observation is similar for the handmade papers which, due to their thicker gauge, means that less of the paper is protected.

As an immediate result of this study, the BL has altered its procedure to include spraying each page from both sides to ensure maximum protection. The Library is now considering whether reducing the moisture content of the paper to aid distribution of the agent is practical and desirable.

## Conclusions

The amount of EMEC distributed over the whole paper sample was fairly consistent for each paper type, but microscopically, however, the EMEC was found to be congealed in large deposits, possibly hydrolysed by moisture in the paper, and not distributed as evenly among the paper fibres as is either desirable or possible. The depth of penetration of the EMEC particles obtained by spraying only one side of the paper is poor for heavy gauged papers and those with a high moisture content, and the thinnest samples retained a relatively low amount of alkaline buffer. The results obtained with the new method of application were similar to those for the previous method, and there was no evidence that the HMDS either reacted with, or remained in, the paper despite the relatively long drying time.

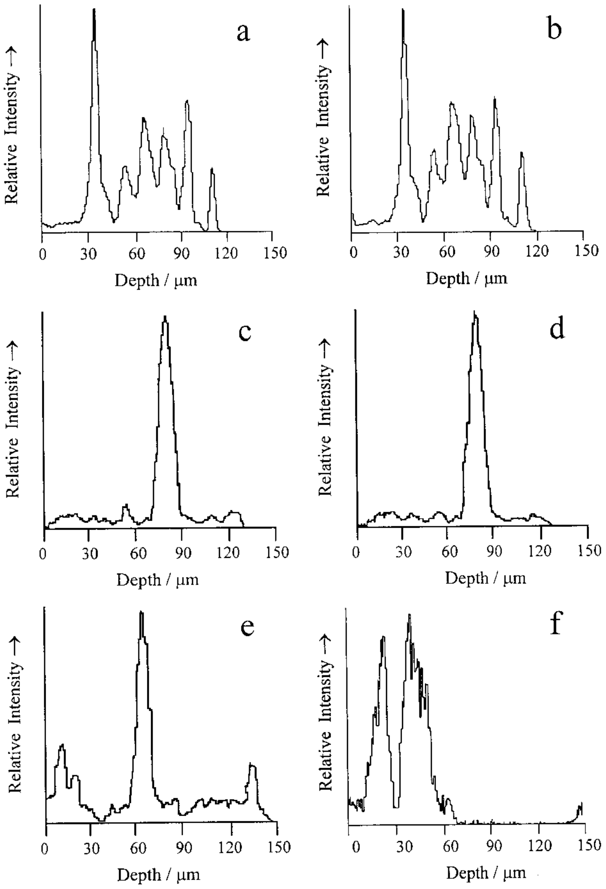


**Fig. 2** PIXE line-scan plots (150 μm) of (a) Al and (b) Si on a general print sample treated with EMEC/HMDS, (c) Ca and (d) S on a general print sample treated with EMEC/HMDS, (e) and (f) Mg on two different samples treated with EMEC/HMDS indicating the lack of penetration through the paper.

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