Solvent extractable components of oil paint films
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6. Measurements of cleaning effects on paintings

Abstract

Experiments were carried out to investigate the extraction of soluble components from paint layers by solvent cleaning treatments, represented by cleaning tests carried out on paintings dating from the seventeenth to nineteenth centuries. Quantities of extractable fatty acids in paint samples taken before and after the local cleaning treatments were determined, and changes in the quantities extractable as a result of cleaning were used to indicate the magnitude of leaching effects. A small, but measurable proportion of the soluble fatty acids was found to be extracted by cleaning in some cases, but in others no significant alterations in the levels of extractable fatty acids were observed. This was despite prolonged cleaning using polar solvents in most of the tests. Some analyses of extracts from cleaning swabs were also carried out.

6.1. Introduction

Measurements of quantities of solvent extractable material from samples from oil paintings dating from the thirteenth to nineteenth centuries were described in Chapter 4, indicating that significant amounts of extractable fatty acids remain in paint layers even after extensive periods of ageing. Furthermore, experiments described in the previous chapter, involving simulated varnishing and cleaning treatments carried out on a test paint film, demonstrated that solvent exposures more typical of conservation practice could result in measurable depletions of components of the oil medium, although the effects were generally at a lower level than those observed in immersion studies.

Generally speaking, these results would suggest that leaching from cleaning or other treatments is a tangible risk even for oil paintings of considerable age. However, it is important to carry out treatment-based experiments on paintings,
get a clearer idea of the magnitude of leaching effects which might be expected in practical situations.

The only detailed study of this type published to date is that of White and Roy [1], which has already been described briefly in Chapter 2. The authors made comparative analyses of samples from a series of paintings, dating from the fifteenth to nineteenth centuries, taken before and after solvent cleaning treatments. GCMS was used to determine the organic composition of the paint samples, and SEM to investigate possible changes in the paint structure, and no evidence was found for chemical or physical changes to paint layers in the cases studied.

As mentioned in Chapter 2, most of the organic analyses as presented in the paper were only semi-quantitative, requiring visual comparisons of paired chromatograms of paint samples before and after cleaning to indicate whether or not changes in the relative proportions of fatty acid components had occurred. It was therefore difficult to make a critical assessment of the data, for which differences were generally stated to be “within experimental error”.

The basis for the chromatographic comparisons is also worth consideration. Paint samples were derivatised for GCMS analysis using the quaternary ammonium reagent TMTFTH (which has also been used extensively in the current study – details of derivatisation methods are given in the following chapter). Chromatograms are obtained from this reagent with peaks corresponding to “total” fatty acids in the sample, i.e. whether these were initially present as free acids, metal salts or glyceride esters. The comparisons made by White and Roy were based partly on the assumption that the more polar, short chain carboxylic acids, particularly the dicarboxylics (azelaiic etc.), would be more susceptible to removal by polar cleaning solvents such as acetone and alcohols [1, pp. 160-161]. Any selective removal of the smaller molecular species should then be evident as a reduced proportion of the corresponding peaks in the chromatogram after cleaning, relative to the larger components such as palmitic and stearic acid. This assumption does not appear to be supported by experimental evidence, however, and conflicts with published studies based on analyses of paint samples and solvent extracts from younger, laboratory prepared paint films, as well as the current study, which indicate that the relatively nonpolar palmitic and stearic acids are generally extracted more readily than dicarboxylics such as azelaic acid, even using polar solvents [2, 3]. In Chapter 4 it was speculated that the lower proportions of azelaic acid found to be extractable from pigmented paint films might relate to the greater potential of this polar, difunctional fatty acid to form ionic interactions with the inorganic (pigment) components of the paint film. From these data, therefore, if any change in fatty acid ratios is to be expected in a paint film as a result of leaching it would more likely be an increase in azelaic relative to palmitic and stearic acids. In any case, the leaching effect would have to be quite pronounced to
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produce a change in fatty acid ratios apparent from a simple visual comparison of chromatograms.

Because of the limitations of this type of analytical comparison, the other parts of the study – analyses of cleaning swabs rubbed gently over exposed paint areas, in which negligible quantities of fatty acids were detected; and SEM comparisons of structural features of paint layers – were more compelling as demonstrations that solvent cleaning was having no significant effects in the cases studied.

With regard to the analysis of swab extracts, measurements of quantities of fatty acids in cleaning swabs were also reported in an earlier study by Ford and Byrne [4], who found variable quantities of palmitic and stearic acid in cotton swabs which had been impregnated with various cleaning agents (including solvents and resin soap gels) and rolled over the surface of an approximately 90 year old, unvarnished oil painting (details of the paint tested, such as pigmentation, were not provided). Quantities extracted were in the order of micrograms fatty acid per cm² paint area, with higher values for strongly alkaline reagents, although the authors acknowledged these values were highly dependent on variable factors (time of exposure, pressure, etc.) inherent in the swabbing procedure. These results are in contrast to the upper limit of nanograms of fatty acids extractable with prolonged exposure to an acetone swab, for a corresponding area of white paint in a sixteenth century painting, which was found by White and Roy [1, p. 163].

Experiments described in this chapter are based on a similar approach of analysing samples from paintings before and after solvent cleaning. Instead of comparing analyses of “total” fatty acids in paint samples, however, measurements have been made of the proportions of solvent extractable fatty acids in each sample, as in Chapter 4, and any differences in these quantities of extractable material in samples before and after cleaning are used to indicate the extent to which leaching has occurred. It is recognised that there will be some natural variation from sample to sample, and multiple samples have been analysed in each case, to account for inherent variations in the chemical composition of the paint layers.

Tests were carried out on a number of paintings dating from the seventeenth to nineteenth centuries, with an aim to measuring quantities of fatty acids extracted from paint layers as a result of solvent cleaning. In some cases, extracts from swabs were also analysed, as an alternative measure of extracted fatty acids.
6.2. Experimental

The paintings used in the study were an early nineteenth century portrait, a fragment from an eighteenth century painting, and several pictures from a seventeenth century group of large scale paintings. Details of these are listed in Appendix 3, and further information on the paint areas tested is given in the results section. All of the paintings were oil on canvas.

The sampling approach consisted of first taking samples from an area of paint which had been cleared of varnish mechanically using a scalpel (this was carried out under a microscope), after which an adjacent area of paint was cleaned thoroughly using solvent swabs in simulation of a cleaning treatment (albeit a thorough one). The paint was allowed to dry, and further samples were taken from the cleaned area. All sampling was carried out in a small area of paint, which was selected to be uniform in its texture, pigmentation, etc. The samples generally consisted of sections through several paint layers, often including ground, and were inspected microscopically before analysis to ensure similarity in terms of size and layer structure. Intact paint fragments of this type were used, rather than scrapings from a single paint layer, as they were more suited to the extraction measurements, typically producing more reproducible results (the difficulty of making extraction measurements using paint scrapings will be discussed further in the results section). This approach does impose certain limits on the interpretations from these experiments, however, as will be discussed later.

Multiple samples were taken — five each “before cleaning” (i.e. from the mechanically cleaned area) and after solvent cleaning. In the extraction experiments described in Chapter 4 for samples from paintings, duplicate samples were generally used, but for these more critical measurements a larger number was used to reduce the likelihood of statistical error as much as possible. (The use of multiple samples is one disadvantage of the method, and limits the extent to which experiments can be carried out on paintings in good condition: the paintings used in this study were either fragments/test pieces, or large scale pictures for which such a sampling protocol was less problematic.)

Each sample was then extracted in solvent for 24 hours — usually the same solvent as was used for cleaning — and the extractable fatty acids quantified using GC. The procedure was the same as that used in Chapter 4, involving separate analyses of the solvent fraction and the extracted paint sample, and is described in detail in Chapter 7. Average results from the measurements before and after cleaning were then compared to determine if any change in the quantities of extractable fatty acids could be observed as a result of the cleaning treatment.
Measurements of cleaning effects on paintings

The examples reported in this chapter have generally used pure acetone or ethanol as cleaning solvents. These represent quite “strong” solvents in terms of general conservation practice, but were chosen initially to test the experimental approach, as they were considered more likely to produce measurable effects than “milder” cleaning treatments.

Swab extract measurements were made on small areas of paint, cleared of varnish mechanically using a scalpel. The exposed paint surface was cleaned using a dry cotton swab, followed by brief surface cleaning with a swab moistened with hexane, to remove any small fragments of abraded paint which might otherwise appear in subsequent swabs as “soluble” material. A small swab of cotton wool, which had been previously cleaned ultrasonically in a sequence of solvents to remove any contaminating fatty acids, was then taken using tweezers, moistened with solvent, and rolled gently over the exposed paint for a given time (typically 10-20 seconds). Factors such as the amount of solvent in the swab and the pressure of application to the paint surface were controlled empirically as far as possible. Care was taken to avoid contamination of the swab at any stage – the cotton wool was only handled using clean tweezers.

After allowing the swab to dry, it was put in a glass vial with 0.5mL of a 2:1 mixture of methylene chloride and ethanol, and extracted ultrasonically for 5-10 minutes. The solvent was transferred to a second vial, a further 0.5mL of the same mixture added to the swab, and the extraction repeated. The choice of this extraction solvent was based on similar mixtures – using chloroform and methanol – which have been shown to be efficient in the extraction of fatty materials in biological applications [5]. Tests using fatty acid standards confirmed the efficiency of extraction using this method.

The combined solvent extract was dried under a stream of nitrogen, with gentle warming, and derivatised for GC using TMTFTH (5% solution in methanol), after the addition of methyl tridecanoate as an internal standard. The solution was left to react overnight, and an aliquot directly injected into the GC. Quantities of fatty acids in the extracts were determined using peak area ratios with the internal standard.

Where possible, pigmentation of the paint areas tested was determined using x-ray fluorescence spectroscopy, or from cross sections using SEM with energy dispersive spectroscopy (EDS).
Chapter 6

6.3. Results and discussion

6.3.1. Analysis of paint samples

The youngest painting tested was an early 19th century American portrait by an unknown artist. As described in Chapter 4, preliminary pigment and medium analysis for this painting indicated a fairly straightforward technique, with conventional pigments bound in pure linseed oil, and no evidence of non-drying additives to the medium. Samples were taken from adjacent locations in an area of flesh paint, consisting of well bound, lead white based paint (also including some vermilion), which had been cleared of varnish using three methods: mechanically cleaned (using a scalpel), cleaned using acetone, and cleaned using an acetone/Sol340HT mixture (2:5). The quantities of fatty acids extractable from these samples in acetone were then determined (fifteen samples were analysed in total – five from each cleaning test area), and results are plotted in Figure 1, with the degree of variation observed within each group of samples indicated. The swabbing in these cleaning tests was prolonged, giving a longer exposure to solvent than would generally be used in practice.

Figure 1  Proportions of palmitic and stearic acids extractable from samples from 19th century portrait, taken from areas of flesh paint cleaned mechanically (A), using acetone (B) and using acetone/Sol340HT (2:5) (C). Samples extracted 24 hours in acetone, results expressed as percentages of total fatty acids in samples.
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The proportions of extractable fatty acids in the paint samples are seen to be reduced in the samples cleaned with acetone (B), and further in those cleaned with acetone/Sol340HT (C), compared to those “before cleaning” (i.e. mechanically cleaned, A). This indicates that a small proportion of the acetone-extractable fatty acids (a few percent relative to total fatty acids in the paint film) has been removed by exposure to these solvents in the form of simulated cleaning treatments. The greater effect of the acetone/Sol340HT treatment may be related to the swelling properties of this solvent mixture (as discussed in Chapter 2, combinations of polar solvents and mineral spirits can have pronounced swelling effects as compared to the pure solvents [6, pp. 90-95]), but it is also likely to be a result of the much longer swabbing which was required with this solvent mixture to remove the oxidised, natural resin varnish.

Values for palmitic and stearic acids only are given in these experiments, since azelaic acid was typically extracted at lower levels, and the results for this compound showed too much variability to allow meaningful comparisons. This is unfortunate, since azelaic acid is a more characteristic marker for drying oil than palmitic and stearic acids, which could conceivably derive from sources other than the oil medium (such as non-drying additives). However, as mentioned above, the ratios of palmitic to stearic acid in the paint samples and extracts studied were consistent with the idea that the extractable material was derived from the linseed oil binder.

Figure 2 shows results from a similar test carried out on an area of black paint (presumably based on a carbon black pigment, but not tested) in the same painting. Adjacent areas of paint were cleared of varnish mechanically (A), and with two acetone cleaning methods. In the first, a series of 10 acetone swabs were rolled over the paint area, one immediately after the other (B). In the other, 10 swabs were also used, but the paint film was allowed to dry thoroughly between each application (C). This was done to test the question of whether a build up of solvent in the paint layer, which would be more likely using method B, could produce a measurable difference in leaching effect. Factors such as the amount of solvent, pressure and time of application of each swab were kept consistent as far as possible.

As in Figure 1, a reduction in the mean proportions of acetone extractable fatty acids can be seen in the samples taken after the two cleaning treatments, compared to those mechanically cleaned. Although the overall quantities of extractable fatty acids are greater in these samples than in the flesh paint samples (around 30-35%, compared to 20-30%), the magnitude of the cleaning effects (as indicated by the differences between the mean extraction values) is smaller. This introduces some ambiguity into the interpretations: although the apparently greater
leaching effect observed for treatment C than for B might seem to contradict the expectation that preventing solvent build up in the paint layer would reduce solvent effects such as leaching, the differences between the groups of samples is small in relation to the degree of variation within the groups. Nothing can therefore be said with confidence about the relative effects of the treatments – the distinction between leaching effects and chance variations between samples in this experiment is less clear. (A more objective statistical treatment of the data will be attempted later in this chapter.) One conclusion which can be drawn is that the application of solvent swabs in rapid succession did not produce a pronounced leaching effect in this case.

Results from an acetone cleaning test on an area of dark green paint (including earth pigments and Naples yellow) in the same picture are shown in Figure 3. The cleaning was thorough, with relatively prolonged exposure to solvent, but despite this a reduction in the quantities of extractable fatty acids in the acetone cleaned samples (B) compared to the mechanically cleaned samples (A) was not observed. A small increase is in fact seen in the mean extraction values after cleaning, but as discussed above, given the inherent range of variation within

Figure 2  Proportions of palmitic and stearic acids extractable from samples from 19th century portrait, taken from areas of black paint cleaned mechanically (A), and using acetone swabs in rapid succession (B) and with drying periods between applications (C). Samples extracted 24 hours in acetone, results expressed as percentages of total fatty acids in samples.
Measurements of cleaning effects on paintings

Figure 3  Proportions of palmitic and stearic acids extractable from samples from 19th century portrait, taken from areas of green paint cleaned mechanically (A) and using acetone (B). Samples extracted 24 hours in acetone, results expressed as percentages of total fatty acids in samples.

the groups of samples, this appears more likely to represent chance variations than a systematic effect.

This result might suggest that the green paint is less susceptible to solvent action than the other areas tested, although it is difficult to generalise based on just one test. (Also, it should be remembered that paint samples used in these experiments included some ground in addition to paint layers, and although the binder for the ground was not determined, it is likely that it is oil based. Some of the extractable fatty acids are therefore likely to derive from the ground, which will effectively diminish any differences in response to solvent associated with the pigmentation of the paint layers.)

One problem with this approach to measuring cleaning effects, analysing samples comprising multiple paint and ground layers, is that the leaching effect measured as a proportion of the whole paint/ground layer structure may be less significant than in the upper paint layers only, where more leaching is likely to occur. Tests were therefore carried out on a fragment of an 18th century painting by an unknown English artist, using a different sampling approach to investigate whether differences in leaching effects could be detected at different depths within the paint layer structure. As in the previous example, initial analyses of paint samples indicated that this painting was made using a pure linseed oil medium,
with no evidence of non-drying additives, and therefore suitable for this type of extraction measurement.

An area of sky paint, lead white based, was cleared of its highly oxidised, discoloured varnish mechanically, and an adjacent area cleaned thoroughly using ethanol swabs. Two groups of samples were then taken from each cleaning test area: the first took the form of whole paint samples, including some ground, as in previous examples; the second consisted of scrapings of the upper paint layers only, excluding any ground material. The samples were then extracted in ethanol (the cleaning solvent in this experiment), and quantities of extractable fatty acids determined as before. Sample sizes for the two types of sample were selected such that approximately equal quantities of fatty acid material were contained in both the scrapings and the whole samples. Care had to be taken in the analysis of paint scrapings, centrifuging after solvent extraction and removing the solvent fraction gently, to avoid transferring small paint fragments in suspension which might distort the apparent quantities of soluble material. (In this example, the paint layers were removable in relatively large fragments. For other paintings, the paint layers could only be separated in the form of very fine particles, which made reliable measurements of soluble material difficult, reflected in erratic and elevated values for the quantities extractable. For this reason, whole paint samples have generally been used in these experiments, despite their limitations.)

Results for the whole paint/ground samples are shown in Figure 4, and for the paint scrapings in Figure 5. Higher extraction values were found for the whole samples (around 40-45%) than for the paint scrapings (20-35%), suggesting that the ground layer contains proportionally more extractable material than the paint layers (again, the binder for the ground was not determined, but it is likely to be oil based, and appears to be mixed with red earth pigments). Reductions in the mean extraction values after ethanol cleaning (B) relative to the mechanically cleaned samples (A) are seen in both cases. The reductions are proportionally greater in the paint scrapings (Figure 5), in which the difference amounts to approximately 15-20% of the total extractable fraction, than in the whole samples (Figure 4), in which the difference represents approximately 8-9% of the total extractables. This would suggest that a greater proportion of material is being extracted from the upper paint layers during cleaning, as compared to the total ground-paint structure, as might be expected from the more direct exposure of the uppermost layers to the cleaning solvent. As in previous examples, however, these results must be interpreted with caution, given the variability exhibited within the groups of samples, particularly the paint scrapings. Additional experiments of this type would be needed to determine if the results are generally representative.
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Figure 4  Proportions of palmitic and stearic acids extractable from whole paint/ground samples from 18th century painting, taken from areas of sky paint cleaned mechanically (A) and using ethanol (B). Samples extracted 24 hours in ethanol, results expressed as percentages of total fatty acids in samples.

Figure 5  Proportions of palmitic and stearic acids extractable from paint scrapings from 18th century painting, taken from areas of sky paint cleaned mechanically (A) and using ethanol (B). Samples extracted 24 hours in ethanol, results expressed as percentages of total fatty acids in samples.
Figure 6  Proportions of palmitic and stearic acids extractable from samples from 17th century painting (Willeboirts-Boschaerts), taken from areas of sky paint cleaned mechanically (A) and using ethanol (B). Samples extracted 24 hours in ethanol, results expressed as percentages of total fatty acids in samples.

Further tests were carried out on a number of paintings dating from the mid 17th century. Figure 6 shows results for an ethanol cleaning test on an area of dark sky paint (lead white based, with carbon black and ultramarine) in a painting by the Dutch artist Thomas Willeboirts-Boschaerts. Data are plotted for ethanol extractable fatty acids from paint samples taken from adjacent locations after mechanical cleaning (A), and after thorough cleaning with ethanol (B). Figure 7 shows results for an acetone cleaning test on a black paint area (with a complex pigment mixture including earths and azurite) in a picture by Cesar van Everdingen, with acetone extraction values after mechanical cleaning (A) and acetone cleaning (B). Both of these pictures are painted on canvas, and are part of the same large-scale group of paintings (see Appendix 3). As in previous examples, the paints were found to be based on a pure linseed oil medium.

Although the solvents are seen to extract considerable quantities of fatty acids from the samples in both cases (35-45% palmitic and stearic acid ethanol extractable in the Willeboirts-Boschaerts samples, and around 25-35% acetone extractable in the van Everdingen samples), the differences between the extraction values for the groups of samples “before cleaning” (mechanically cleaned) and after solvent cleaning are small in both cases, in relation the degree of variation inherent in the measurements. Again, no clear conclusions can be drawn about the
Measurements

Measurements of cleaning effects on paintings

Fig 7 Proportions of palmitic and stearic acids extractable from samples from 17th century painting (van Everdingen), taken from areas of black paint cleaned mechanically (A) and using acetone (B). Samples extracted 24 hours in acetone, results expressed as percentages of total fatty acids in samples.

extent of leaching – this is particularly true in these cases in which only one cleaning test was carried out. Any effects there might be are too small to be reliably measured using this method.

In some additional experiments of this type, the degree of precision found in the extraction measurements was so poor as to prevent any reasonable interpretations being made about cleaning effects. This is presumably a result of some paint films being less chemically homogeneous than others, and therefore less suited to this type of comparative experiment. In addition, for paint samples that showed low levels of extractable material, it was correspondingly more difficult to make accurate comparative measurements. Some cases in which extraction measurements showed a high degree of variation have therefore been omitted from this chapter.

6.3.2. Statistical analysis of data

The experiments have been interpreted above in fairly general terms, based on visual assessments of the plotted extraction data. A more objective evaluation
can be made using statistical tests to compare the groups of results in the various experiments.

A standard procedure for assessing the significance of the difference between the means of two groups of data is the $t$ test. This involves a calculation of the $t$ ratio, which is the difference between the means of the two groups divided by an estimate of the standard error of the difference between the means. (Formulae for estimating the standard error of the difference, and for calculating the $t$ ratio, are given in Appendix 4.) Calculated $t$ ratios are then compared with critical values of $t$, obtained from standard tables. If the calculated $t$ ratio is greater than the critical value (or less, for negative values), this suggests a systematic effect (in these examples, a solvent leaching effect), whereas if it is smaller, the difference observed is more likely to be a result of chance variation (resulting from inhomogeneity in the paint film, as well as experimental error – these factors will be addressed in more detail in Chapter 7).

To obtain critical $t$ values, a significance level must be selected for the test. Typically a 5% level is used, which in effect means that the probability of the calculated $t$ ratio being above the critical value as a result of chance alone, without a systematic effect, is less than 5%. More or less rigorous significance levels can also be used, the main difference being the strength of the conclusions which can be drawn: determining a significant difference at a 1% level is more convincing than at a 5% level, and at a 10% level it is less persuasive. Significance levels greater than 10% are not generally used.

Table 1 lists $t$ ratios calculated from the extraction data for palmitic acid in the experiments described above, and plotted in figures 1-7. In the table, $X_1$ and $s_1$ are the mean and standard deviation for the percentages palmitic acid extractable from samples before cleaning, $X_2$ and $s_2$ are the corresponding values for the samples after solvent cleaning, $s_{X_1-X_2}$ is the estimated standard error of the difference between the means, and $t$ is the $t$ ratio calculated for each experiment (see Appendix 4 for details). The significance level is denoted by $\alpha$, expressed as a fraction. Critical $t$ values for the conditions of this experiment are $\pm 1.86$ at a 10% level, $\pm 2.31$ at a 5% level and $\pm 3.36$ at a 1% level. Hence, experiments with $\alpha$ listed as 0.01 (for which $t>3.36$) would be considered to demonstrate a leaching effect at a 1% significance level or greater (i.e. the chance of the difference observed between the means resulting from chance factors alone is less than 1%). A $\alpha$ value of 0.1 (for experiments in which $2.31>t>1.86$) denotes that a leaching effect is signified at the 10% level, and $\alpha>0.1$ gives no strong indication of a leaching effect: taken on an individual basis, the results of such experiments are quite likely just to represent chance variations.
Measurements of cleaning effects on paintings

Table 1  Calculations of t ratios for cleaning test data: percentages palmitic acid extractable from paint samples before cleaning (1) and after cleaning (2).

<table>
<thead>
<tr>
<th>sample</th>
<th>solvent</th>
<th>$X_1$</th>
<th>$s_1$</th>
<th>$X_2$</th>
<th>$s_2$</th>
<th>$s_{X1,X2}$</th>
<th>t</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C19, flesh paint</td>
<td>acetone</td>
<td>28.0</td>
<td>1.86</td>
<td>25.4</td>
<td>2.32</td>
<td>1.33</td>
<td>1.96</td>
<td>0.1</td>
</tr>
<tr>
<td>C19, flesh paint</td>
<td>ac/Sol $^1$</td>
<td>28.0</td>
<td>1.86</td>
<td>23.6</td>
<td>1.39</td>
<td>1.04</td>
<td>4.24</td>
<td>0.01</td>
</tr>
<tr>
<td>C19, black paint</td>
<td>ac (fast) $^2$</td>
<td>34.1</td>
<td>2.37</td>
<td>32.6</td>
<td>3.76</td>
<td>1.99</td>
<td>0.75</td>
<td>&gt;0.1</td>
</tr>
<tr>
<td>C19, black paint</td>
<td>ac (slow) $^3$</td>
<td>34.1</td>
<td>2.37</td>
<td>31.5</td>
<td>1.46</td>
<td>1.24</td>
<td>2.09</td>
<td>0.1</td>
</tr>
<tr>
<td>C19, green paint</td>
<td>acetone</td>
<td>36.8</td>
<td>1.63</td>
<td>38.7</td>
<td>4.25</td>
<td>2.04</td>
<td>-0.93</td>
<td>&gt;0.1</td>
</tr>
<tr>
<td>C18, sky (whole)</td>
<td>ethanol</td>
<td>42.6</td>
<td>3.55</td>
<td>38.9</td>
<td>1.88</td>
<td>1.80</td>
<td>2.06</td>
<td>0.1</td>
</tr>
<tr>
<td>C18, sky (scraping)</td>
<td>ethanol</td>
<td>29.9</td>
<td>5.09</td>
<td>25.5</td>
<td>2.09</td>
<td>2.46</td>
<td>1.79</td>
<td>&gt;0.1</td>
</tr>
<tr>
<td>C17, dark sky paint</td>
<td>ethanol</td>
<td>39.3</td>
<td>4.43</td>
<td>41.2</td>
<td>1.70</td>
<td>2.12</td>
<td>-0.90</td>
<td>&gt;0.1</td>
</tr>
<tr>
<td>C17, black paint</td>
<td>acetone</td>
<td>32.3</td>
<td>3.97</td>
<td>29.2</td>
<td>4.28</td>
<td>2.61</td>
<td>1.19</td>
<td>&gt;0.1</td>
</tr>
</tbody>
</table>

$^1$ acetone/Sol340HT, 2:5  
$^2$ acetone, swabs applied in rapid succession  
$^3$ acetone, paint allowed to dry between swab applications

A number of the results in Table 1 support the initial, empirical interpretations: data from cleaning tests in the flesh paint area of the 19th century portrait, illustrated in Figure 1, provide evidence for a leaching effect by acetone cleaning (at the 10% significance level), and strong evidence for leaching by prolonged cleaning with acetone/Sol340HT (at the 1% significance level). Evidence for a leaching effect is also found for the second acetone cleaning test in the black paint area of the same painting (Figure 2, treatment C), and in the ethanol cleaning test on the 18th century painting fragment (from the analysis of whole paint samples – Figure 4), both using the 10% significance level. In all other examples, there was no strong evidence for a systematic (leaching) effect.

It should be stressed that these statistical tests are only aids to interpretation, and the nature of the individual experiments must also be taken into account. For example, statistical analysis of the cleaning tests on the 18th century fragment provide evidence of a leaching effect from the analysis of whole paint samples ($t>1.86$), but not from the analysis of paint scrapings ($t<1.86$), even though the mean change observed in the latter case was proportionally greater. This is a result of the poorer precision (i.e. the greater degree of variability) found in the analysis of paint scrapings, as discussed in the previous section, resulting in a lower $t$ ratio for this experiment. Similarly, it seems unlikely that the cleaning test on the black paint of the 19th century portrait using acetone swabs in rapid succession would have a lesser effect than the same treatment with drying periods between swab applications, as might be inferred from the $t$ ratios. As discussed before, the different results in this case are more likely to represent experimental variations. (A $t$ test can in fact be carried out to compare the extraction data after
cleaning, from both methods, instead of comparing results from samples before and after cleaning. This analysis gives a $t$ ratio of 0.61, well below the 10% significance level, supporting the idea that there is very little difference between the effects of the two treatments.)

In cases where only one cleaning/sampling procedure was used, as for the 17th century paintings, the information which can be drawn from the results is limited, and the $t$ tests are more useful in supporting empirical assessments of the data – in these cases, reinforcing the idea that the cleaning treatments have had no significant effect.

6.3.3. Analysis of swab extracts

As an alternative method of measuring extractable fatty acids, solvent swabs were rolled over exposed areas of flesh paint (cleared of varnish mechanically) in the 19th century portrait, as described in the experimental section. Four solvents were used: xylene, methylene chloride, acetone and ethanol; with duplicate swabs for each. Each area of paint, approximately 5 x 5mm, was exposed to a swab for 15 seconds. After extraction and derivatisation of the material from each swab, chromatograms were obtained which, in addition to fatty acid methyl esters, included a number of peaks corresponding to variable amounts of residual varnish components (identities of specific compounds were not determined, but the region of the chromatogram in which these peaks elute, after methyl stearate, is characteristic of natural resin components). This indicates that the mechanical clearance of varnish had not been completely efficient. Illustrative chromatograms for extracts from a xylene and a methylene chloride swab are shown in Figure 8, showing that methylene chloride removes a considerable amount of the residual varnish components, and xylene very little. The fatty acid peaks were clearly resolved from these additional components, however, and could be measured in relation to the internal standard.

The quantities of fatty acids detected in the swab extracts are plotted in Figure 9, with averages plotted for duplicate swabs in each case. Fatty acids were detected in the order of fractions of micrograms per swab. It is difficult to relate these results quantitatively to the cleaning test data because of the different experimental methodologies. However, from the analysis of paint samples from the same area of the painting it can be estimated that a 1mm$^2$ sample (comprising several layers, including ground) contains approximately 2.5μg total palmitic acid, corresponding to 62.5μg in a 5 x 5mm area. The maximum value of 0.31μg palmitic acid found in the methylene chloride swabs is therefore likely to represent approximately 0.5% of the total amount of this compound in the paint film.
Figure 8  Gas chromatograms of extracts from swabs applied with xylene (a) and methylene chloride (b) to mechanically cleaned areas of flesh paint in 19th century portrait. Az = dimethyl azelate, P = methyl palmitate, S = methyl stearate, IS = internal standard: methyl tridecanoate. Peaks eluting later in the chromatogram correspond to residual varnish components.

Because of the variability inherent in the swabbing procedure, this calculation can only be considered very approximate. Very little azelaic acid was detected in the swab extracts, further indication that this compound is less readily extractable from paint layers than palmitic and stearic acid, as discussed in the introduction.

In terms of the relative effects of the different solvents, these results are in agreement with the total quantities of fatty acids extractable from samples from the same paint area by immersion in solvent, described in Chapter 4 (Figure 10a), with the greatest quantities of fatty acids found in the methylene chloride swabs, followed by ethanol, acetone and xylene. This is despite the additional variable factors – including rates of diffusion and evaporation – which are absent from the "total" extraction measurements, and might be expected to influence the swabbing results.
Similar analyses were made of swabs from a mid 17th century painting by Pieter Soutman (part of the same group of paintings as the Willeboirts-Boschaerts and van Everdingen described in previous sections), from a number of paint areas with different pigmentation. Ethanol swabs were used in each case, otherwise experimental parameters were as before. In these cases, quantities of fatty acids detected were very low, in the same order as background levels found in blank swab extracts, and so could not be measured with any precision. (Despite precautions such as thorough cleaning of the cotton wool, the analysis of swab extracts is difficult to execute cleanly, and some degree of background contamination is unavoidable. This can also result from the concentration of the large volumes of solvent used for extraction. It is important to run blank samples for this reason.) The low levels of fatty acids in swabs from the Soutman correlate with the cleaning tests on the other two 17th century paintings, in which changes in the quantities of extractable fatty acids from cleaning were too small to be reliably measured.

One exception in the case of the Soutman was a swab from an area of vermilion paint, which was found to contain relatively high levels of fatty acids. The chromatogram for the swab extract is shown in Figure 10. This paint area was clearly vulnerable to ethanol, as indicated by the appearance of pigment on the swab, and so the result represents an unusual case – with fatty acids derived from disintegration of the paint medium, rather than a leaching effect. The high proportion of azelaic acid in the extract (with an azelaic/palmitic ratio of 2.7) is an
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![Gas chromatogram of extract from swab applied with ethanol to mechanically cleaned area of vermilion paint in 17th century painting (Soutman). Az = dimethyl azelate, P = methyl palmitate, S = methyl stearate, IS = internal standard: methyl tridecanoate.](image)

**Figure 10** Gas chromatogram of extract from swab applied with ethanol to mechanically cleaned area of vermilion paint in 17th century painting (Soutman). \(Az = \) dimethyl azelate, \(P = \) methyl palmitate, \(S = \) methyl stearate, \(IS = \) internal standard: methyl tridecanoate.

Indication of the catalytic effect of this pigment on the oxidative degradation of the oil polymer.

### 6.4. Conclusions

In cleaning tests carried out on a number of paintings from the seventeenth to nineteenth centuries, in which quantities of extractable fatty acids were measured in paint samples before and after cleaning, a small, but measurable proportion of fatty acids was found to be removed from the paint layers in some cases, whereas in others the effect was too small to be reliably determined. This was despite the use of polar solvents, and prolonged exposure to swabs in most cases.

In general, these results reinforce the idea that the extent of leaching occurring as a result of a superficial exposure to solvent, as in cleaning, is likely to be very small in relation to the total amount of material extractable by immersion in solvent. This supports the observations made by White and Roy [1], although in their study no significant changes from cleaning were observed in any of the cases.
investigated, and the conclusions drawn were correspondingly more comprehensive.

It should be re-emphasised that this research is concerned with the leaching of organic components from an otherwise coherent paint film. More immediate, obvious risks relating to the vulnerability of specific paint types – illustrated above by the swab extract from the vermilion paint, in Figure 10 – are a separate issue, relating to peculiar drying properties of the paint, as discussed in Chapter 1.

Given the magnitude of effects observed, and the time consuming nature of the analyses, it was not possible to make an extensive investigation of the influence of factors such as pigmentation and age of the paint films, and different solvent treatments, using this type of measurement. For example, although greater effects were observed on the nineteenth century painting than on the eighteenth and seventeenth century paintings, this difference cannot be reasonably attributed to the age of the pictures based on so few examples. The particular techniques and materials used in oil painting in the different periods may also be important factors in this respect. Similarly, it was not possible to distinguish between solvent effects on lead white based paint films and those which might be expected to show a greater vulnerability to leaching, such as black pigmented films. (In part, this is likely to be a result of the “homogenising” effect of ground layers in the paint samples analysed.)

For information on the effects of these various factors, it is necessary to rely on the studies of model paint films described in previous chapters, which are more suited to this type of controlled comparison, but bearing in mind that the effects of immersion treatments on these younger paint films are exaggerated in relation to the more practical cleaning situations.

The results can perhaps be more usefully interpreted in relation to questions as to the effects of solvent cleaning on paintings which have already undergone a number of previous cleaning treatments. As Ruhemann asked:

*Will not the maximum leaching have already occurred in most old pictures during the many and harsh cleanings they have undergone in the past? Will not therefore most varnish removals be carried out nowadays without risk of further leaching? [7, p. 305]*

Erhardt and Tsang later raised similar questions:

*It is not known ... whether [leaching] occurs only during the first cleaning of a painting, occurs for several cleanings and eventually stops, or will occur to some extent during every cleaning.* [2, p. 93]
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Although the paintings tested in this study cannot be taken to represent those which have had “many and harsh cleanings”, the results would seem to contradict the idea that any leachable material present in paint layers will be removed in initial cleanings, and that subsequent treatments are unlikely to have any further effect. Given that, at least in the cases studied, there is a considerable “reservoir” of extractable material in paint films even of significant age, and that an individual cleaning treatment appears to remove only a very small proportion of the total extractable, it seems more likely that leaching is a phenomenon which occurs, although at a low level, on each repeated exposure to solvent. Moreover, results described in Chapter 4 indicated that extractable material can continue to form in a paint film as a result of ongoing ageing processes.

Hence, although an individual cleaning treatment may present a minimal risk to the paint layers from leaching, it is still important to avoid frequent re-treatments as far as possible. To a large extent, this view supports conventional wisdom in cleaning.

An additional factor investigated in this chapter was the magnitude of leaching at different depths in the paint layer structure. Measurements of quantities of solvent extractable fatty acids in different types of sample from the eighteenth century painting (whole paint/ground samples and paint scrapings) suggested that leaching was more pronounced in the surface layers, although more data, and more precise methods of analysis, would be needed to support this observation. Since the uppermost paint layers are the most critical in terms of the appearance of the painting, this is an area which deserves further investigation. More detailed investigations of the mechanical and optical effects associated with leaching, as a result of solvent exposures more typical of practical situations, would also be valuable.

References


