

Analyzing the effect of diethylaminoethanol, an indoor air pollutant, on traditional easel paintings

**IUAM DEAE* Analysis Project Final Report for Phase 1:
Analytical Procedures for DEAE In DEAE Contaminated Paintings
(*DEAE: diethylaminoethanol)**

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CCI Service Request No. CPMR 693

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Executive Summary

Results

1. Traces of DEAE were detected by GC analysis of water swabs from 4" x 5" areas of the acrylic glazing on "Salon Rose Roix". The amount detected was about 1.7 ng of DEAE per square millimeter of acrylic surface. This is about 18 times less than the amount detected on surfaces at Johnson Museum, Cornell University, when analyzed in 1983 (30 ng per square meter).
2. DEAE was possibly detected by GC analysis at CCI of large cleaning swabs from "Swing Landscape" by Stuart Davis, and "Madame Chinnery". The swabs analyzed were old ones taken more than a year prior to CCI involvement in the project and are ten to 100 times larger than swabs taken by Williams in 1996. They were not stored in air-tight containers and volatile components may have been lost. Barrett-Wilt (Chemistry, IU) detected DEAE in the swabs from "Swing Landscape" by GC analysis in 1994 and 1995.
3. DEAE was possibly detected by GC analysis at CCI of 1.1 mg of dust from the back of "Peinture" by Soulages Barrett-Wilt detected DEAE by GC analysis.
4. No DEAE was detected by GC analysis of water swabs from small, 3 mm x 3 mm, areas of painting surfaces from "Ste Catherine" or "Magdalen Reading".
5. No DEAE was detected by GC analysis of relatively large samples from "Blue Sky" (water swab from 16 mm x 13 mm area, or 0.5 mg scraping of varnish surface from 3 mm x 4 mm area) or "Green Trees" (water swab from 12 mm x 13 mm area, or 0.7 mg of scraping from paint surface from 4 mm x 5 mm area). These painting fragments had been exposed to steam humidified air containing DEAE in air conditioning vents at Lilly Library.
6. No DEAE was detected by GC analysis of any dry swab from any object sampled.
7. No free, unreacted DEAE was detected by FTIR analysis of samples from any painting. However, "Blue Sky" and "Green Trees", exposed at Lilly Library, and "Beach Scene" and "Portrait of Leila in Red" by Engel, showed some spectral characteristics that are similar to reaction products produced in the laboratory by direct addition of liquid DEAE to samples of varnishes and paints from various paintings. These reaction products have IR spectra that are different from material not treated with DEAE. The reaction products may be esters formed by reaction of carboxylic acids in the varnish and paint media with the alcohol group of DEAE (DEAE esters), or substituted ammonium carboxylate salts formed by reaction of carboxylic acids with the nitrogen in the amine group of DEAE (DEAE carboxylates,

analogous to reaction of ammonia with acids).

8. IR spectroscopy indicates that "Ste Catherine" and "Magdalen Reading" contain water sensitive or water soluble materials like starch and protein DEAE or its reaction products were not detected on these paintings. In these paintings, hazing and other problems ascribed to contamination by DEAE might be due to the presence of these water soluble materials in or on the paints and varnishes.

9. DEAE is a very good solvent for varnish resins and oil paints. When fragments of paintings were suspended in the vapor above a few drops of DEAE in a closed vial, the varnish absorbed so much DEAE vapor that the varnish dissolved and dripped off the fragment, and the paint became very soft.

10. Liquid DEAE dissolves fresh dammar and aged danimar varnish film dating from 1948, and when this varnish/DEAE solution is cast on glass and allowed to sit in air, a hard film like a typical varnish film is formed.

Conclusions

1 FTIR microspectroscopy is the best method to survey the paintings in the IUAM collection for the presence of DEAE and its reaction products. This method requires the smallest sample (particles much less than 1 mm in diameter) and provides the most information in a single analysis (medium and pigment composition, DEAE and reaction products, information from different layers, etc) The GC method provides only a yes or no answer for the presence of DEAE.

2. Small amounts of DEAE esters and DEAE carboxylates, the reaction products of DEAE with varnish resins and oil paint media, but not free DEAE itself, were detected by FTIR microspectroscopy of particles measuring 50 μm (0.05 mm) in diameter. This is much smaller than the size of sample that is normally considered acceptable for sampling for chemical analysis.

3. DEAE cannot be detected in dry swabs or water moistened swabs from areas less than about 30 mm x 30 mm by the GC technique used in this analysis The minimum area required to be swabbed in order to obtain a detectable amount of DEAE has not been determined conclusively, but areas measuring 4" x 5" (100 mm x 125 mm) on the acrylic glazing of "Salon Rose Roix" yielded a just barely detectable amount of DEAE so this would appear to be close to the area limit.

4. DEAE and its reaction products are present in small concentrations on some surfaces, in some accretion layers, in some varnish layers, or in some paint layers, of some paintings in the IUAM collections The amounts present are very small and do not appear to be uniformly distributed since they are not detected in all paintings.

5. No sample analyzed appears to have been significantly changed by the presence of DEAE reaction products, although these products may be responsible for some of the effects attributed to DEAE contamination.

6. In some paintings, water soluble components in or on the varnishes and paints, rather than DEAE reaction products from DEAE contamination, may be the prime cause of abnormal behaviours observed when some paintings are swabbed with water moistened swabs.

Recommendations for further work

The results of these analyses indicate that DEAE and its reaction products are present on some paintings. Some of the effects attributed to DEAE contamination may be due to the presence of water soluble components like starch or protein (glue, egg, etc.). Since the number of paintings examined for this report is so small, a true picture of the extent of the DEAE problem cannot be drawn. More paintings should be analyzed.

FTIR microspectroscopy is the quickest, most informative, and least intrusive technique to use for this analysis.

To clarify the extent of the effects of DEAE and the mechanism of its interaction with paintings the following further work is recommended:

1. Minuscule samples should be taken of varnishes and paints from many paintings that are apparently subject to DEAE contamination problems, for analysis by FTIR microspectroscopy, specifically for the presence DEAE esters and DEAE carboxylates, and for the presence of water soluble or water sensitive materials like starch and protein. This should quantify the number of paintings that are affected by DEAE and the extent of the DEAE problem.
2. Test samples or model paintings should be exposed to DEAE vapors then analyzed by FTIR microspectroscopy to clarify the chemical reactions between painting media, DEAE, and DEAE reaction products. This has already been done to some extent in developing the FTIR microspectroscopic analysis procedure. The additional work needs to use more realistic exposure conditions such as exposure to a DEAE/air mixture of about 1% DEAE, rather than pure DEAE vapors or immersion in liquid DEAE This would determine whether the interactions under less severe exposure conditions are the same as at the higher concentrations used in the FTIR analysis.
3. Test samples or model paintings should be analyzed by microscopical methods, before and after exposure to DEAE, and before and after cleaning treatments to determine the physical or structural effects of DEAE exposure and subsequent cleaning of DEAE exposed paintings.
4. The analysis reported here has shown that for some paintings, wiping with water moistened swabs removes water soluble compounds from the painting, including starch and protein ("Ste Catherine") and DEAE reaction products ("Green Trees"). Additional tests should be made to determine if swabbing with water moistened swabs is an effective treatment for removal of DEAE reaction products DEAE reaction products are polar compounds and therefore soluble in polar solvents like water and alcohols. They are also surface active agents and therefore may be soluble in nonpolar solvents like aliphatic and low aromatic hydrocarbons such as mineral spirits or naphtha. Alkanolamine soaps such as those

produced by reaction of monoethanolamine (MEA) with coconut or tall oil fatty acids show some solubility in these solvents. Analogous DEAE soaps with the increased hydrocarbon content due to substitution of the two hydrogens on the nitrogen of MEA by two ethyl groups will be even more soluble in these solvents. The effects of using these solvents to remove DEAE reaction products should be investigated. Using nonpolar solvents that may be less damaging to paintings than water, may be a valuable alternative procedure.

1. Introduction

This Final Report on Phase 1 of the IUAM DEAE Analysis Project (CCI Service Request No CPMR 693) describes in detail the work performed by the Canadian Conservation Institute (CCI) for the Indiana University Art Museum (IUAM) on Phase 1 of IUAM Contract Proposal No 44877, Account No 43-200-27, for the IUAM project entitled "Investigation into the Effects and Removal of DEAE on Painting Media", conducted under Grant No MT-0424-5-NC-013 from US Department of the Interior, National Parks Service.

The IUAM DEAE Project is under the direction of Margaret Contompasis, Painting Conservator, IUAM. R. Scott Williams, Conservation Scientist (Chemist), Conservation Processes and Materials Research Section is the principle investigator for CCI.

The research objectives of the IUAM DEAE Project, as listed in Attachment A of the Contract, are:

- 1) To determine if DEAE can penetrate the surface of the coated and uncoated paintings.
- 2) To determine if, following penetration, DEAE reacts physically or chemically with the painting surface, and how those changes will affect subsequent cleaning.
- 3) To determine if DEAE can be safely removed from the varnish or paint surface using conventional solvent systems.

The purpose of the CCI work, as described in Attachment A of the Contract, is to provide specific scientific analytical services, namely:

- 1) To determine if DEAE is present on the surface, in accretion layers, in varnish layers, or in paint layers of paintings in the IUAM collections that have been exposed to humidified air containing DEAE.
- 2) To determine whether painting surfaces and layers have been changed by DEAE.
- 3) To determine whether DEAE can be removed safely from varnish or paint surfaces using conventional solvent treatments.

The CCI work is being carried out in two phases, with Phase 1 to establish appropriate analytical procedures for determining the presence and effects of DEAE on paintings, and Phase 2 to analyze the effects of DEAE and conservation treatments on DEAE contaminated paintings.

Phase 1 included the following tasks, as listed in Attachment A of the Contract.

- 1) Examination of paintings in the IUAM collection that are apparently affected by DEAE contamination, and taking samples for analysis.
- 2) Analysis of samples of surfaces, accretions, varnish and paint from DEAE contaminated paintings to determine most suitable techniques for detecting the presence of DEAE on paintings and characterizing the physical structure of the DEAE contaminated paintings
- 3) Preparation of a report which summarizes the findings of Phase 1 investigations,

and recommends the analytical procedures that should be used for subsequent investigations.

CCI has submitted two previous Progress Reports (September and October, 1996) summarizing development work and results. This Final Report incorporates, and supersedes, these previous Progress Reports. Submission of this Report fulfills the obligations of CCI for Phase 1 of the IUAM DEAE Analysis Contract.

2. Examination of paintings at IUAM

Scott Williams visited IUAM during the week of July 13-19, 1996. With Margaret Contompasis and Danae Thimme, paintings and other objects on display at the Art Museum and the Lilly Library of Indiana University were examined, in situ, with the naked eye. During this examination the phenomenon attributed to contamination by DEAE from the humidification system was observed. The phenomenon appeared primarily as a disruption of gloss in the form of a bluish film or haze on the surface of paintings, most noticeable over dark colored areas.

Additional paintings were examined more closely in the conservation laboratory by microscopical methods. A second phenomenon attributed to DEAE contamination was observed on these paintings. When some paintings are swabbed with water moistened swabs in areas showing the bluish film or haze, the film is removed, and the area develops a whitish hazed appearance. Continued swabbing with water moistened or saliva moistened swabs removes the hazed appearance from the area, and restores the healthy appearance to the varnish or paint film.

Samples were taken from these paintings by Scott Williams and Margaret Contompasis for chemical analysis at CCI.

3. Sample selection and collection

Samples consisted of wipings on small cotton swabs, powders and particles obtained by scraping the surface of the painting, or particles or flakes excised from the painting with a scalpel. Samples were taken from areas of paintings that showed effects attributed to the presence of DEAE such as hazy or greasy appearing surfaces, varnishes that became abnormally hazy or milky when swabbed with water, etc.

Cotton for swabs was prewashed with methanol. Swabs were prepared by wrapping a small wad of cotton batting around the tip of stainless steel forceps. Gloves were worn when wrapping the swabs to prevent transfer of fingerprints. The swabs measured about 2 mm diameter by 5 mm length. Wipings were done either with dry swabs or with deionized water moistened swabs. After wiping the surface the swabs were removed from the forceps and stored in glass vials closed with teflon/silicone septa with the teflon side facing inwards.

Scrapings were made by dragging a scalpel across a prescribed area of the painting surface in such a manner that only a single layer was removed, and usually only the upper surface of that layer. The operation was carried out while observing with a stereomicroscope. Scrapings were removed with the scalpel or a needle and transferred either to septum capped

glass vials or microscope slides. Samples on microscope slides were covered with another microscope slide then the two slides were taped together to trap the sample between them.

Particles or flakes were excised from the painting surfaces using a scalpel, then transferred and stored in septum capped glass vials.

Additional samples, taken by others more than a year prior to Williams' visit, were supplied by Margaret Contamipasis. These samples consisted of water moistened swabs and powders brushed from the surfaces of paintings. They have not been stored in air-tight containers. Some of these samples were analyzed by gas chromatography at the Chemistry Department of Indiana University by Greg Barrett-Wilt (1996).

All samples are described in **Appendix A**.

4. Methods of Analysis

4.1. Thermal Desorption/Gas Chromatography/Mass Spectrometry (TD/GC/MS)

Several methods of analysis of DEAE and other tertiary amines by different analytical techniques have been published. Gas chromatographic methods use direct injection onto the GC column of underivatized DEAE in aqueous solutions (ASTM D 4983-89; Malaiyanda and Goddard, 1990), underivatized DEAE in organic solutions (Lester and White, 1967), and silylated derivatives of DEAE in organic solution (White and Swafford, 1973); desorption from adsorbent gas sampling traps (Fannick, et al, 1983; Visscher, 1990); or direct injection of gas samples into special GC apparatus (Edgerton, et al., 1989). Liquid chromatographic methods rely on formation of colored or radioactive derivatives (Michelot, et al., 1983), as do spectrophotometric and colorimetric methods (Larrick, 1963; Miller, et al., 1967). Only the publications of Fannick, et al (1983) and Visscher (1990) DEAE with the analysis of DEAE in museums, and both use gas adsorbent trap - GC methods. The GC methods are most sensitive and convenient. For this project a thermal desorption (TD) method of sample introduction onto a GC column was chosen. This TD method is a modification of one that has been used for several years at CCI for GC/MS analysis of volatile compounds emitted by paints and adhesives.

The TD method involves two steps which are carried out in a Thermal Desorption Unit (TDU). In the first step, the sample preparation or loading mode, a sample of either gas or liquid is injected through a septum into a sample tube, an empty 1/4" OD glass tube, contained in a temperature controlled tube chamber, then the tube chamber sample preparation heating program is activated. Carrier gas flowing through the sample tube, sweeps the volatilized sample out of the sample tube onto an adsorbent tube which is a 1/4" OD, 1 mm ID glass tube packed with adsorbents (Carbotrap 301) that adsorb efficiently organic molecules having a size greater than equivalent to alkanes with about 2 to 3 carbon atoms (i.e., compounds with molecular weights greater than about 30-45 atomic mass units, amu). Thus, water, oxygen, carbon dioxide, and methanol, for example, pass through the adsorbent tube without being adsorbed, whereas larger molecules such as DEAE (MW =117 amu) are completely adsorbed in the adsorbent tube. By this means, small amounts of DEAE can be concentrated in the adsorbent tube by injecting large volumes of methanol

solution (e.g., 5 μ L) into the sample tube.

In the second step, the desorption mode, the adsorbent tube with the adsorbed analyte is placed in the tube chamber. Carrier gas flow through the tube is switched from the path to the adsorbent tube to the path through the GC column. The temperature of the tube chamber is raised rapidly to 330 C to desorb the sample from the adsorbent tube and the desorbed sample is swept through the GC where separation and subsequent detection with the mass spectrometer occurs.

One advantage of this TD sample injection method is that concentration of the DEAE in methanol extracts by evaporation of the methanol is not necessary, so there is no loss of DEAE by simultaneous evaporation, or azeotropic distillation. Another advantage is that, since most of the methanol passes through the adsorbent tube, no methanol is injected onto the analytical column when the sample is desorbed so there is no large background signal in the chromatogram due to methanol solvent. Contaminants in the methanol are concentrated so high purity solvent is required.

All swabs were extracted with methanol added directly to the sample vial, typically 0.5 mL which was just sufficient to cover the swabs in the vials For gas chromatographic analysis, samples of the extract were removed from the vial by a syringe pierced through the septum in the vial cap then injected into the thermal desorption unit.

Powder and flake samples stored in vials were extracted, dissolved, or dispersed in methanol, typically 0.25 to 0.5 mL, by addition of methanol directly to the vial. Samples of these liquids were removed from the vial by a syringe pierced through the septum in the vial cap.

To prevent loss of volatile DEAE or its reaction products, all samples collected during Williams' visit were kept in septum sealed glass vials, except for the brief period when methanol was added to the vial Also no methanol solutions or mixtures were subjected to evaporation to concentrate the samples

The TD/GC/MS apparatus and instrument settings were as follows:

Gas Chromatograph/Mass Spectrometer Hewlett Packard (HP) 5870 GC with a HP 5970B Mass Selective Detector (manual dated January 1986) controlled by a HP 59970C MS ChemStation with HIP 59974J GC/MS Software (revision 3.1.1, copyright 1986) using a HP 9133H Disc Drive.

GC Column: DB-WAX, 30 m x 0.25 mm ID x 0.25 μ m film thickness (J&W Scientific, P/N 122-7032) received on 16/8/94.

GC Oven: 45°C for 2 min, then to 200°C at 20°C/min and hold.

Thermal Desorption Unit: Dynathenn Analytical Instruments, inc. Thermal Desorption Unit (TDU) Model 890/891 from Supelco, Inc.

TDU Adsorbent Trap: Carbotrap 301 Multibed Thermal Desorption Tube, 1 mm ID (Supelco Catalog No. 2-0354).

Split Ratio at TDU exit. 60:40 (column:vent)

TDU Temperature Conditions:

Preparation (loading) mode: initial approx 45°C, final 300°C, 4 min hold.

Desorption mode: initial: approx 45°C, final: 330°C, 4 min hold.

Injection Volume (typical): 5 µL of methanol extract or solution using a Hamilton 701 syringe.

4.2. Fourier Transform Infrared (FTIR) Spectroscopy

A few individual particles from powdery scrapings or excised chips and flakes were analyzed by Fourier transform infrared spectroscopy using a Spectra-Tech IR-Plan lit microscope interfaced to a Bomem MB-120 FTIR Spectrometer.

Samples were prepared in a low pressure diamond anvil sample cell from High Pressure Diamond Optics by placing a particle on one anvil, assembling the cell, then squeezing the sample by applying pressure until the sample was about 10 µm thick. The diamond cell was opened and the anvil with the sample stuck to it was mounted in the IR microscope for spectroscopy of circular areas of the squeezed samples measuring 100 µm in diameter, using clear areas of the diamond anvil immediately adjacent to the sample for background spectra for each sample spectrum.

The typical sample size was about 10 µm thick by 100 µm in diameter. Assuming that the density of the sample is about 1 gm/cm³, the weight of the sample analyzed can be calculated:

$$\begin{aligned}
 &10 \mu\text{m} \times \pi \times (50 \mu\text{m})^2 = 10 \times 3.14 \times 50 \times 50 = 78450 \mu\text{m}^3 \\
 &= 7.8\text{E}4 \mu\text{m}^3 \times (1 \text{ cm} / 10^4 \mu\text{m})^3 \\
 &= 7.8\text{E}-8 \text{ cm}^3 \\
 &= 7.8\text{E}-8 \text{ cm}^3 \times 1 \text{ gm}(\text{sample})/\text{cm}^3 \\
 &= 7.8\text{E}-8 \text{ gm}(\text{sample}) \\
 &= 78 \text{ ng}(\text{sample})
 \end{aligned}$$

FTIR spectroscopy is usually capable of detecting components in mixtures that comprise 1% or more of the total sample weight when there is no overlap of absorption bands for the components. DEAE has absorption bands that are not masked by absorption bands of resin and acrylic varnishes or oil and protein paint media. Thus the limit of detection for DEAE in painting samples by this FTIR microspectroscopic technique should be about 1% of 78 ng or 0.78 ng DEAE.

When the sample is on the diamond anvils it can be treated with reagents by placing drops of reagents on the sample as it rests on the diamond, allowing these to react and then evaporate, then acquiring spectra of the dry reaction products.

This procedure has been used for years at CCI to remove lead and calcium carbonates from samples by adding hydrochloric acid (which reacts with the carbonate to produce carbon dioxide gas and IR transparent calcium or lead chlorides) or to remove silica and silicates by adding hydrofluoric acid (which produces volatile silicon tetrafluoride and IR transparent metal fluorides).

The judicious addition of hydrochloric acid or sodium or ammonium hydroxide in various

sequences can also be used to probe carboxylic ester, acid, and salt functional groups. For example, the presence of a carboxylate salt (e.g., zinc stearate) can be confirmed by observing the shift of the Zn carboxylate absorption from 1540 cm^{-1} to 1710 cm^{-1} for carboxylic acid when hydrochloric acid is added. Subsequent addition of sodium hydroxide causes the 1710 cm^{-1} peak of acid to disappear while the $1580\text{-}1540\text{ cm}^{-1}$ peak for sodium carboxylate salt (soap), appears.

The effects of DEAE on the IR spectra of samples was investigated by placing a drop of DEAE on the sample after an initial spectrum of the untreated material had been obtained. These reactions were observed using a stereomicroscope. The process of evaporation of the DEAE was observed and in some cases hastened by the heat from the illuminating lamps. Reaction products with the DEAE were subsequently treated with water, mineral acids, and alkalis to observe their reactions. Spectra of the reaction products were acquired.

4.3. Freeze fracture experiments and scanning electron microscopy (SEM)

5 mm wide strips were cut from the test paintings using a sharp scalpel yielding test pieces about 5 mm wide x 50 mm long. The test pieces were immersed in liquid nitrogen (LN2). Immediately after removal from the LN2 the test pieces were bent around a 5 mm diameter metal rod to fracture the paint layer. The support layer did not fracture and was cut with a scalpel. Two pieces of each test piece resulted. One piece has been stored in a glass vial as a control. The other piece has been suspended by a thread in a vial over 1 mL of pure DEAE. These were to be examined by scanning electron microscopy (SEM).

5. Results of Analysis

The results of all TD/GC/MS analyses are presented in **Appendix B**. The results for FTIR spectroscopic analysis are presented in **Appendix C**. These results are discussed here in detail for each of the objects sampled.

5.1. Analysis of DEAE reference samples and boiler treatment products

The mass spectrum and IR spectrum of DEAE reference material, Aldrich Catalog No 24004-4 (N,N-Diethylethanolamine, 99+ %), agree with published spectra.

The mass spectra and lit spectra of boiler treatment products are identical to the reference material. Only DEAE was detected by GC analysis.

5.1.1. Lower limit of detection by TD/GC/MSD of DEAE dissolved in methanol

To determine the sensitivity of the TD/GC/MS method, solutions of Aldrich DEAE in methanol were analyzed. The results are listed in **Appendix B**. Using injection volumes of $5\text{ }\mu\text{L}$ of solution, DEAE in methanol at 50 ppm (v/v) has been detected with an 86 amu (atomic mass unit) ion peak height of about 20000. DEAE has a density of 0.88 g/mL , therefore,

$$\begin{aligned}
& 50 \text{ ppm (v/v)} \\
& = 50 \times 10^{-6} \text{ mL(deae)/mL(soln)} \\
& = 50 \times 10^{-6} \text{ mL(deae)/mL(soln)} \times 0.88 \text{ g(deae)/mL(deae)} \\
& = 44 \times 10^{-6} \text{ g(deae)/mL(soln)} \\
& = 44 \text{ }\mu\text{g(deae)mL(soln)} \\
& = 44 \text{ }\mu\text{g(deae)/mL(soln)} \times 10^{-3} \text{ mL}/\mu\text{L} \\
& = 44 \times 10^{-3} \text{ }\mu\text{g(deae)}/\mu\text{L(soln)} \\
& = 44 \text{ ng(deae)}/\mu\text{L(soln)}.
\end{aligned}$$

5 μL of 50 ppm DEAE in methanol produced a distinct total ion chromatogram (TIC) peak in the gas chromatogram and a mass spectrum of DEAE at the retention time of the peak maximum for this peak. The same volumes of 10 and 16 ppm DEAE in methanol produced small TIC peaks with peak height only 2 or 3 times the background noise and mass spectra missing ions at 117 amu and sometimes at 102 amu which are normally found in mass spectra of DEAE. Thus the lowest limit of detection under these conditions is about 5 μL of 50 ppm DEAE in methanol or 5 $\mu\text{L(soln)} \times 44 \text{ ng(deae)}/\mu\text{L(soln)} = 220 \text{ ng(deae)}$, based on the 86 amu ion peak height when the ions at 102 amu and 117 amu are also present.

5.1.2. Comparison of GC analysis of headspace gases versus liquid extracts

An initial effort was made to analyze the headspace gas above samples stored in sealed vials, to determine if any DEAE had been emitted by the samples. DEAE was not detected in 1 mL samples of headspace in any swabs, scrapings or flakes from painting or other surfaces and this procedure was abandoned. Either the procedure is not sufficiently sensitive to detect the low concentration of DEAE that may be present (i.e., less than 220 ng of DEAE per mL of air in the vial), or the DEAE is contained in the samples in an involatile form that does not evaporate into the headspace in sufficient concentration to be detected.

5.2. Samples taken by Williams

Swabs from the surface of the acrylic glazing on the poster "Salon Rose Roix" hanging on the IUAM painting storage rack

The results for this object are discussed first, since these samples are from the largest area of any object sampled and are most likely to have DEAE, if the exposure of the "Salon Rose Roix" in storage was the same as the other objects on display.

The acrylic sheet was covered with a dusty and greasy appearing film. Single dry and water moistened swabs were wiped across the acrylic sheet over four different areas measuring about 4" x 5" each. In Area 1, dry swabs were used first, followed by water moistened swabs. In Areas 2, 3 and 4, a water moistened swab was used first, followed by dry swabs to wipe up water droplets.

These swabs were extracted with 0.5 mL methanol. 5 μL of the extract was analyzed by TD/GC/MS.

Only water moistened swabs removed detectable amounts of DEAE, but only a just barely

detectable amount. Wiping areas as large as 4" x 5" with dry swabs does not remove detectable amounts of DEAE even though this wiping appears to move material around on the surface.

Comparison of the 86 amu ion peak heights for the water moistened swab extracts with those of the DEAE/methanol solutions shows that the concentration of the DEAE in the swab extract is about 50 ppm = 44 ng(deae)/ μ L(soln). From the total volume of the extract (0.5 mL = 500 μ L) and the area of the acrylic wiped (4" x 5" = 20 in²) the amount of DEAE per unit area of surface of acrylic can be calculated:

$$\begin{aligned} & 44 \text{ ng(deae)/}\mu\text{L(soln)} \times 500 \mu\text{(soln)} \\ & = 22000 \text{ ng(deae)} \\ & = 22000 \text{ ng(deae)} / [20 \text{ in}^2 \times (25.4 \text{ mm/in})^2] \\ & = 1.7 \text{ ng(deae)/mm}^2\text{(acrylic)} \end{aligned}$$

The amount of DEAE per unit area of surface of the acrylic is 1.7 ng/mm².

FTIR spectroscopy of the deposits on the swabs, or of material removed from the acrylic glazing, was not performed.

Swabs and scrapings from the surface of "Ste. Catherine" by Francesco Zagnelli (IUAM 77.43)

Small areas of the painting which showed a hazy, milky, or greasy appearing surface deposit were swabbed over areas about 3 mm x 3 mm, using small dry or water moistened swabs. Scrapings of the varnish and tiny flakes of paint were taken from these areas, before and after swabbing. All swabs were extracted with 0.5 mL of methanol then analyzed by GC, and the solids were analyzed by FTIR.

No DEAE was detected in any of the swabs or powdery scrapings by GC. The total area wiped was 9 mm². If the painting has the same amount of DEAE per unit area as the acrylic sheet then we expect a total of 9 mm² x 1.7 ng/mm² = 15.3 ng(deae) to be in the 0.5 mL of methanol extract. This is 15.3 ng(deae) / 500 μ L(soln) = 0.0306 ng(deae)/ μ L(soln) which is about 1000 times less than the minimum detectable concentration of DEAE by this TD/GC/MS technique. If there is DEAE in the paint layer, not just on the varnish layer, then the amount of DEAE available for removal by the swabbing might be higher.

Several particles of varnish scraped from the surface (samples 3, 3-1, 10, and 11) and paint from under the varnish (sample 13) were analyzed by IR spectroscopy. IR spectra of the varnishes are very similar to aged dammar and show mainly absorptions for carboxylic acids (1700 cm⁻¹) but not esters (1735 cm⁻¹).

Varnish taken before the surface had been wiped with water moistened swabs (Samples 3 and 3-1), have additional absorptions which may be attributed to starch or other similar carbohydrate (absorptions at 1030 cm⁻¹ from C-O-C bonds). Samples 10 and 11, varnish taken after the surface had been wiped with water moistened swabs, do not have carbohydrate. It is possible that carbohydrate was initially present as in sample 3, but that

this water soluble component was removed by wiping with water moistened swabs.

Addition of DEAE to the varnish causes the varnish to disperse completely, with most of it dissolving, leaving only a trace of undissolved gelatinous material. DEAE converted the varnish acids (1710 cm^{-1} to esters (1735 cm^{-1}), presumably by a reaction between the alcohol group of the DEAE and the acid groups of the varnish resin. The 1030 cm^{-1} band, attributed to carbohydrate is not affected. The gelatinous material which is not dissolved by DEAE may be the carbohydrate, the source of the 1030 cm^{-1} band. The 1030 cm^{-1} band did appear to be more abundant in sample 3 which had the gelatinous material than in samples 10 and 11 which did not, supporting this hypothesis.

There is no indication in the IR spectra that DEAE is present in the varnish. The presence of the carbohydrate may be responsible for the haziness observed when the painting is treated with water. Water may swell and dissolve the carbohydrate from the varnish, disrupting the layer sufficiently to cause optical changes. The disappearance of the haziness when the hazy area is swabbed with saliva, but not with water, may be due to the replenishment of the lost carbohydrate by the involatile components of the saliva (enzymes and other proteins, mucins (glycoproteins), and carbohydrates, etc.), which are not present in water which is consequently ineffective in reducing the hazing.

Sample 13, a flake of varnish and paint taken before swabbing with water, contains carboxylic acids (1707 cm^{-1}) but no ester (1735 cm^{-1}), plus protein ($1652/1535\text{ cm}^{-1}$) which may be glue or egg, carbonate (lead or calcium, not determined) and barium sulfate. The carbonates were removed by reaction with hydrochloric acid as described above. This treatment also removed the protein peaks. The carbonate free sample was reacted with DEAE This converted the acid (1707 cm^{-1}) to ester (1735 cm^{-1}) and regenerated the protein peaks ($1655/1567\text{ cm}^{-1}$). Further treatment of this with hydrochloric acid converted some of the ester to acid and once again removed the protein peak. The barium sulfate was unaffected by all reagents.

There was no evidence in the IR spectra that DEAE was present in the paint, unless the $1650/1560\text{ cm}^{-1}$ peaks which were attributed to protein were actually DEAE reaction products. This latter is unlikely since several separate experiments where resins, fatty acids, and esters were reacted with DEAE did not produce the $1650/1560\text{ cm}^{-1}$ pair. These are much more likely due to protein.

The presence of a water sensitive or soluble material, the protein, may be responsible for the hazing behaviour when the painting is treated with water moistened swabs, in the same manner as described for Sample 3.

Swabs and scrapings from "Magdalen Reading" by Master of the Female Half-Lengths (IUAM 77.12.1)

GC analysis of methanol extracts of dry and water moistened swabs, and solid scrapings of varnish and paint, did not detect any DEAE.

IR spectroscopic analysis of the varnish on "Magdalen Reading" showed that it is composed

predominantly of resin acids, typical of resin varnishes like dammar. As in the case of “Ste. Catherine” there appears to be an admixture of a small amount of carbohydrate like starch. The spectrum of varnish from a water swabbed area is almost indistinguishable from that of a varnish that has not been treated. There is little or no reduction in the carbohydrate after water swabbing, contrary to what was observed for “Ste Catherine”.

The IR spectrum of paint taken from an area after the varnish had been scraped away has the typical pattern (fingerprint) of ortho-phthalate alkyd, i.e., alkyd paint. It is definitely not a typical vegetable drying oil. There are several other weak but sharp peaks in the spectra that are reminiscent of the patterns obtained from red organic pigments. Their increased intensity in portions of the sample that are deeper red in color supports the attribution of these peaks to red organic pigments.

The area where this sample was taken should be examined to see if it is an overpainted area. Otherwise IUAM may have the earliest example of use of alkyd paint.

Solid scrapings from “Beach Scene” by Harry Engel

The spectra of waxy orange paint and the waxy brown paint are nearly identical to that of zinc stearate. All the peaks present in zinc stearate spectrum are present in the sample spectra. The slight differences in the spectra of the two colors may be attributed to absorptions from different pigments.

Addition of DEAE to these paints caused them to dissolve or disperse. The DEAE evaporates away to leave a dry reaction product. The carboxylate peak of the zinc stearate (1540 cm^{-1}) is considerably reduced and a new peak at 1592 cm^{-1} appears. The ester (1735 cm^{-1}) appears to be unaffected. Since the 1592 cm^{-1} peak was not initially present in the medium before treatment with DEAE, it is most likely that it is from a reaction product of DEAE with the carboxylate. The formation of esters by reaction of DEAE with paint and varnish media has been described above. However, carboxylic esters usually absorb around 1735 cm^{-1} whereas carboxylate salts absorb in the range $1500\text{-}1600\text{ cm}^{-1}$. Thus the band at 1592 cm^{-1} is more likely from a carboxylate salt than an ester.

In the presence of sufficient water, DEAE is most likely present in a protonated form, analogous to the ammonium ion from ammonia in water. This protonated DEAE may react with carboxylic acids to produce a DEAE carboxylate salt, in the same way the ammonium ion reacts with carboxylic acids to form ammonium carboxylate salts. Ammonium carboxylates have carbonyl absorptions in the range $1600\text{-}1550\text{ cm}^{-1}$ (citrate and oxalate: 1600 cm^{-1} , tartrate- 1576 cm^{-1} , acetate- 1568 cm^{-1}). Apparently some zinc carboxylate (1540 cm^{-1}) has been converted into a protonated DEAE carboxylate salt (1592 cm^{-1}). When the DEAE reaction product is treated with hydrochloric acid, the ester (1735 cm^{-1}) the DEAE carboxylate salt (1592 cm^{-1}), and the unreacted zinc carboxylate (1540 cm^{-1}) are converted to carboxylic acid (1710 cm^{-1}). These ester/acid/salt conversions at different acidities are typical reactions for these functional groups and have been observed often in analyses where oil paint samples have been reacted with mineral acids and alkalis, in this manner.

A medium that is so rich in zinc carboxylate soap is a very unusual paint medium. Zinc

carboxylate has been used in oil paints supplied in tubes to help prevent the pigment from settling and caking (Mayer, 1981) but it is not used at such high concentrations for this purpose. Such high concentration of carboxylate soap would tend to give a very weak film that would be easily smeared or wiped off. This would behave very differently from a normal oil or acrylic paint, and this different behaviour may be erroneously attributed to effects of DEAE contamination.

Solid scrapings from “Portrait of Leila in Red” by Harry Engel (IUAM 71.86.8)

The varnish on this painting is a clear, colorless, elastic film. It cannot be scraped, but can be peeled off the underlying paint. The spectrum of a fragment that was peeled off very closely matched the spectrum of poly(butyl methacrylate), a commonly used acrylic varnish obtainable from many sources (Williams, 1994).

When DEAE was added to this varnish, the varnish completely dissolved then redeposited as a film within minutes as the DEAE evaporated. The spectrum of the redeposited film was identical to the untreated material. Although there is dissolution, there is no apparent permanent chemical reaction between the poly(butyl methacrylate) varnish and DEAE.

There is no evidence in the IR analysis for the presence of DEAE or any reaction product of DEAE with the poly(butyl methacrylate) varnish.

IR spectroscopy of the brown paint shows it is predominantly a mixture of carboxylic acid and ester, perhaps a mixture of oil and varnish resin. It also contains a significant proportion of protein ($1636/1537\text{ cm}^{-1}$), perhaps egg or glue, perhaps as much as 25%. The presence of the protein may give this paint abnormally high sensitivity to water. Barium sulfate is also present, but not calcium or lead carbonate.

This paint dissolved or dispersed a bit in DEAE, but not as much as did resin and acrylic varnishes, or the zinc carboxylate paints.

Addition of DEAE to this paint results in a decrease in the intensity of the ester/acid peak ($1735/1710\text{ cm}^{-1}$) and the appearance of a strong peak at 1592 cm^{-1} . Peaks at 1460 , 1402 , 1320 cm^{-1} become more prominent. This is the same reaction as for Sample 16 of “Beach Scene” but occurred to a much greater extent in “Leila”. When hydrochloric acid is added to the DEAE reaction product the 1592 cm^{-1} peak disappears and an acid peak at 1709 cm^{-1} reappears, as in “Beach Scene”.

The behaviour of the “protein” at $1632/1537\text{ cm}^{-1}$ is different to what was expected DEAE caused the 1537 cm^{-1} peak to disappear but not 1632 cm^{-1} . Normally these two peaks behave as a pair, both increasing or decreasing in unison. Their separate behaviour suggests that these peaks might not indicate protein.

Swabs from acrylic strip dated 11/9/87

This sample is an acrylic strip that was put “on display”, suspended by a wire, in the gallery

on 11/9/87. It currently has a hazy coating on both sides. Methanol moistened swabs were wiped across areas measuring 35 mm x 35 mm. No DEAE was detected by GC analysis of methanol extracts of these swabs. The deposit was not analyzed by IR spectroscopy.

Solid scrapings from fragments of paintings exposed in air conditioning diffuser vent at Lilly Library

“Blue Sky”

An area measuring 3 mm x 4 mm, and weighing 0.5 mg was scraped from the surface of the painting, then dissolved in 0.5 mL of methanol. An area measuring 16 mm x 13 mm was wiped with two consecutive water moistened swabs and these were extracted together with methanol. GC analysis of these solutions did not detect DEAE in either scraping or swab.

There is no varnish on “Blue Sky”. IR spectra of blue paint show ester, typical of drying oil (but not like an acrylic), barium sulfate, and a small amount of carbonate (calcium or lead, not determined). There is also a strong peak at 1587 cm^{-1} which is typical of aluminum carboxylate salts, such as aluminum stearate or aluminum palmitate. These are used in paints in the same way as zinc stearate, as indicated in the discussion of result for “Beach Scene”. This may also be a protonated DEAE carboxylate, as discussed for “Beach Scene”.

Addition of DEAE does not cause significant dispersion of the sample and does not change the spectrum. This suggests that if DEAE reacts with the paint, it did so completely while the paint was exposed. When treated with hydrochloric acid, ester (1735 cm^{-1}) and carboxylate (1587 cm^{-1}) disappear while carboxylic acid (1712 cm^{-1}) appears. Carbonate is also destroyed. Addition of DEAE to the hydrochloric acid reaction product regenerates the ester (1735 cm^{-1}) and a very broad peak about $1600\text{-}1610\text{ cm}^{-1}$. This behavior with DEAE and HCl is like that described for “Beach Scene” and “Portrait of Leila in Red”.

“Green Trees”

An area measuring 4 mm x 5 mm, and weighing 0.7 mg was scraped from the surface of the painting, then dissolved in 0.5 mL of methanol. An area measuring 12 mm x 13 mm was wiped with two consecutive water moistened swabs and these were extracted together with methanol. GC analysis of these solutions did not detect DEAE in either scrapings or swabs.

This painting has a thick yellow varnish. The lit spectrum of this varnish is very similar to “Dammar March 1948”, a film of dammar varnish cast on glass in 1948, in the CCI collection. There is no glue present in the varnish. The spectrum has a broad strong band at 1716 cm^{-1} perhaps with a shoulder at around 1600 cm^{-1} which may be carboxylate salt like that previously discussed. This possible carboxylate peak is orders of magnitude less intense in this sample than in the oil paint for “Blue Sky”, in accordance with the observation that the carboxylates are most prevalent in oil, not resin, media.

Addition of DEAE produces a reaction product with a new and very different spectrum. The acid (1707 cm^{-1}) is reduced and a strong peak at 1572 cm^{-1} is produced. The appearance of the band at 1572 cm^{-1} suggests a protonated DEAE carboxylate salt has been formed

analogous to that formed from zinc stearate. The slightly different frequency of the absorption (1572 cm^{-1} instead of 1592 cm^{-1}) may be because resin acids (terpenic acids) are different from fatty acids which may cause slight frequency shifts for the salts. The reaction product after subsequent treatment with HCl has a spectrum nearly identical to the original untreated (but exposed) varnish, as it should be for a protonated DEAE carboxylate.

The reaction of DEAE with the varnish sample suggests that the reaction of varnish with DEAE during the time of exposure in the Lilly Library had not gone to completion. This may be because the varnish is very thick and there simply is more of it to be reacted than in the case of the paint of "Blue Sky", which appeared to have reacted to completion.

An area of the varnish was vigorously scrubbed with a water moistened swab, then a spectrum of the varnish was obtained. This spectrum was very nearly identical to varnish from an untreated spot, but the shoulder at about 1600 cm^{-1} which is in the untreated varnish is absent from the water swabbed varnish. The 1600 cm^{-1} peak is tentatively attributed to a protonated DEAE resin carboxylate soap. The behaviour towards water indicates its solubility and the potential that it will be extracted by water moistened swabs, which may lead to hazing. It is reasonable to expect the DEAE resin carboxylate to be water soluble.

5.3. Samples taken by others

More than a year before CCI involvement in the DEAE project, samples consisting of water moistened swabs and powders brushed from the surfaces of paintings had been taken for analysis at the Chemistry Department of Indiana University (Barrett-Wilt, 1996). These swabs and powders were analyzed for this report. These samples have not been stored in air-tight containers.

Cleaning swabs from "Madame Chinnery"

Small amounts of DEAE was detected by GC analysis at CCI in methanol extracts of some, but not all, swabs from "Madame Chinnery".

Cleaning swabs from Mylar on back of "Swing Landscape" by Stuart Davis Powder from "Peinture" by Soulages (70.86)

Gas chromatograms obtained by CCI of methanol extracts of the swabs from "Swing Landscape" by Stuart Davis, and methanol solutions of the powder from "Peinture" by Soulages, had a weak peak at a retention time greater than that of reference DEAE, and also had a mass spectrum with some but not all of the characteristic ions for DEAE. A very small amount of DEAE may have been present. However, the poor match of retention time and mass spectrum with DEAE standards indicates that this is unlikely.

Barrett-Wilt (1996) detected DEAE by GC analysis in swabs from "Swing Landscape" (sample GBW0054, 30 Nov 96 and sample GBW0008: S.18 "Stuart Davis #2 surf dirt", 7 Jun 95) and in powder from "Peinture" (GABW0009, 4 Apr 96).

Cleaning swabs from “Interior of Church” by E. DeWitte

Cleaning swabs from “Portrait of a Lady” by Terborch

Powder from “La Fenetre” by Balthus (70,62)

No DEAE was detected by GC analysis at CCI in the methanol extracts of the swabs from “Interior of Church” by DeWitte or “Portrait of a Lady” by Terborch, or in methanol extracts of powder from “La Fenetre” by Balthus.

Barrett-Wilt but did not detect DEAE in powder from “La Fenetre” (GABW0008, 4 Apr 96). Barrett-Wilt’s results for “Madame Chinnery”, “Interior of Church” and “Portrait of a Lady” were not available for comparison.

Powder from “tie Ring”

This sample, consisting of powder sandwiched between two microscope slides, labelled “de Ring”, was analyzed by FTIR spectroscopy. Its spectrum matches a copolymer of vinyl acetate with a few percent of ethylene (less than 5% ethylene). It was not analyzed by GC.

5.4. Freeze fracture and DEAE incubation for SEM examination

Strips of “Horses” (Research Painting #3) and “Sea Scape” (Research Painting #5) were cooled in liquid nitrogen to make them brittle then fractured by bending over a metal rod. One piece of each fractured strip was suspended in a glass vial above a few drops of DEAE. When examined 23 days after being set up, it was observed that the varnish on “Horses” has absorbed so much DEAE that it had dissolved and the solution had dripped off the painting. The green and brown colors had also severely faded or in some other way degraded. The strip of “Sea Scape” had bent and in so doing come into contact with the side wall of the vial where it had stuck. The paint layer was wrinkled and soft. No SEM analysis was done.

6. Discussion of Results

The amount of DEAE per unit area of surface of the acrylic glazing on “Salon Rose Roix” was determined to be 1.7 ng per square meter. Fannick, et al (1983) reported that they found 30 mg of DEAE per square meter of exposed surface from their analysis of “bulk samples” of plastic film that had been exposed to the atmosphere of the Johnson Museum, Cornell University “for years”. 30 mg of DEAE per square meter is $30 \text{ mg/m}^2 \times 10^6 \text{ ng/mg} \times 10^{-6} \text{ m}^2/\text{mm}^2 = 30 \text{ ng(deae)/mm}^2$ or an amount roughly 18 times greater than that observed on the glazing of “Salon Rose Roix”.

Very little free, unreacted DEAE was found on any surface. This is not surprising. DEAE is a volatile liquid. A drop on a microscope slide evaporates to dryness in about 1 minute. Only if it reacts with compounds in the painting will it be present, and then, only as a “fixed”, involatile reaction product.

There does appear to have been some reaction of DEAE with varnish and paint media.

There appear to be two mechanisms operating. In one, the alcohol group of the DEAE reacts with acid groups in the media to produce esters (DEAE esters). In the other, the nitrogen of the amine group in DEAE reacts with the acid groups in the media to produce substituted ammonium carboxylate salts (DEAE carboxylates).

There is a complex interaction between DEAE, acids, esters, and carboxylate salts in the medium, and acidic or basic reagents added to the medium during treatment. This interaction is not yet clear, but the following is probably true. The DEAE esters are not likely to be water soluble, whereas the DEAE carboxylate salts probably are. Any medium that has a significant concentration of DEAE carboxylate salt may be affected abnormally by water.

Although the small amounts of DEAE reaction products detected may be responsible for some of the subtle effects attributed to DEAE contamination, no sample analyzed has chemically reacted very much with DEAE, and in those samples where DEAE reaction products were found, only relatively small amounts of these were present.

Samples from some paintings contain water soluble or water sensitive components such as carbohydrates and proteins, which are unrelated to DEAE contamination. In these paintings, the effects attributed to DEAE contamination might be due to the presence of the water sensitive components.

No SEM examination was carried out during this work. Upon reflection, SEM examination did not seem to be an appropriate technique to determine damage caused by DEAE contamination. While it may be possible to characterize the current structure of surfaces or cross-sections of paintings, this will only give a snap-shot of the current state of the paintings. This will not permit any assessment of changes caused by exposure to DEAE because we have no data on the structure of the paintings before DEAE exposure for comparison. SEM or other microscopical analysis may be of some use in determining how treatments change the structure, but in the absence of data on how the painting would respond if it had not been exposed to DEAE, changes observed cannot be directly related to the effects of DEAE.

7. Conclusions

1. FTIR microspectroscopy is the best method to survey the paintings in the IUAM collection for the presence of DEAE and its reaction products. This method requires the smallest sample (particles much less than 1 mm in diameter) and provides the most information in a single analysis (medium and pigment composition, DEAE and reaction products, information from different layers, etc). The GC method provides only a yes or no answer for the presence of DEAE.
2. Small amounts of DEAE esters and DEAE carboxylates, the reaction products of DEAE with varnish resins and oil paint media, but not free DEAE itself, were detected by FTIR microspectroscopy of particles measuring 50 μm (0.05 mm) in diameter. This is much smaller than the size of sample that is normally considered acceptable for sampling for chemical analysis.

3. DEAE cannot be detected in dry swabs or water moistened swabs from areas less than about 30 mm x 30 mm by the OC technique used in this analysis. The minimum area required to be swabbed in order to obtain a detectable amount of DEAE has not been determined conclusively, but areas measuring 4" x 5" (100 mm x 125 mm) on the acrylic glazing of "Salon Rose Roix" yielded a just barely detectable amount of DEAE so this would appear to be close to the area limit.
4. DEAE and its reaction products are present in small concentrations on some surfaces, in some accretion layers, in some varnish layers, or in some paint layers, of some paintings in the IUAM collections. The amounts present are very small and do not appear to be uniformly distributed since they are not detected in all paintings.
5. No sample analyzed appears to have been significantly changed by the presence of DEAE reaction products, although these products may be responsible for some of the effects attributed to DEAE contamination.
6. In some paintings, water soluble components in or on the varnishes and paints, rather than DEAE reaction products from DEAE contamination, may be the prime cause of abnormal behaviours observed when some paintings are swabbed with water moistened swabs.

8. Recommendations for further work

The results of these analyses indicate that DEAE and its reaction products are present on some paintings. Some of the effects attributed to DEAE contamination may be due to the presence of water soluble components like starch or protein (glue, egg, etc.). Since the number of paintings examined for this report is so small, a true picture of the extent of the DEAE problem cannot be drawn. More paintings should be analyzed.

FTIR microspectroscopy is the quickest, most informative, and least intrusive technique to use for this analysis.

To clarify the extent of the effects of DEAE and the mechanism of its interaction with painting the following further work is recommended:

1. Minuscule samples should be taken of varnishes and paints from many paintings that are apparently subject to DEAE contamination problems, for analysis by FTIR microspectroscopy, specifically for the presence DEAE esters and DEAE carboxylates, and for the presence of water soluble or water sensitive materials like starch and protein. This should quantify the number of paintings that are affected by DEAE and the extent of the DEAE problem.
2. Test samples or model paintings should be exposed to DEAE vapors then analyzed by FTIR microspectroscopy to clarify the chemical reactions between painting media, DEAE, and DEAE reaction products. This has already been done to some extent in developing the FTIR microspectroscopic analysis procedure. The additional work needs to use more realistic exposure conditions such as exposure to a DEAE/air mixture of about 1% DEAE, rather than pure DEAE vapors or immersion in liquid DEAE. This would determine

whether the interactions under less severe exposure conditions are the same as at the higher concentrations used in the FTIR analysis.

3. Test samples or model paintings should be analyzed by microscopical methods, before and after exposure to DEAE, and before and after cleaning treatments to determine the physical or structural effects of DEAE exposure and subsequent cleaning of DEAE exposed paintings.

4. The analysis reported here has shown that for some paintings, wiping with water moistened swabs removes water soluble compounds from the painting, including starch and protein ("Ste. Catherine") and DEAE reaction products ("Green Trees"). Additional tests should be made to determine if swabbing with water moistened swabs is an effective treatment for removal of DEAE reaction products. DEAE reaction products are polar compounds and therefore soluble in polar solvents like water and alcohols. They are also surface active agents and therefore may be soluble in nonpolar solvents like aliphatic and low aromatic hydrocarbons such as mineral spirits or naphtha. Alkanolamine soaps such as those produced by reaction of monoethanolamine (MEA) with coconut or tall oil fatty acids show some solubility in these solvents. Analogous DEAE soaps with the increased hydrocarbon content due to substitution of the two hydrogens on the nitrogen of MEA by two ethyl groups will be even more soluble in these solvents. The effects of using these solvents to remove DEAE reaction products should be investigated. Using nonpolar solvents that may be less damaging to paintings than water, may be a valuable alternative.

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Appendix A: Samples for analysis from Indiana University Art Museum objects

Object: “Ste. Catherine” by Francesco Zagnelli (IUAM Acc. No. 77.43)

Information transcribed from Accession Card (see Labbook, p. 43):

H11¼” x W8¼”

Thinly applied oil with ; of surface for loss. Sept 9, 1984: thin layer of grime, fingerprints, needs to be cleaned or surface dusted. Feb 1993: varnish is dulled with grime & streaked possibly with DEAE film. Discolored retouch or crack @ left.

Scott Williams’ observations (transcribed from Labbook, p. 43):

Discrete unattached or unimbedded “dust” particles everywhere distributed at about 1-5 mm intervals, generally white and spherical, not fibrous.

Surface film is not very distinct and does not badly disrupt appearance. However, swab test with water immediately causes hazing of varnish. Varnish is perceptibly thick - top and bottom require slight refocus to view at 50x.

Samples from lower left in dark background just above beige bar. Samples taken of varnish – See notes of sampling recorded by Margaret Contompasis.

Photo after Sample 4, taken at 15, 30, and 60 sec using microscope lights. I believe magnification setting was 12X. Photometer set at DF (Dark Field).

Sample information transcribed by Scott Williams from photocopy of notes recorded by Margaret Contompasis

Samples taken by Scott Williams, 17 July 1996

Sample 0:

cotton batting used for all sample swabs

(Vial: #0 - Methanol washed cotton)

Sample #1:

Spot 1, 7.8 x 1.0 cm LLC [lower left corner], light dusting, (skimmed surface)

(Vial: #1 - Dust)

Sample #2:

same area, burnished, abraded, two-three mm, light scrub of surface (try to remove freckle from surface of varnish), scratched

(Vial: 2 - dry swab, burnished, abraded, 3x3 mm):

Sample #3

Chip of varnish, same area, collected onto microscope slide w/ scalpel, varnish is v. brittle

Sample #4:

Widening of varnish sample by scraping, Bubble, Consecutive slices exposed an airspace(?) in varnish - scraping w/ probe suggests it is a hole

(Vial: 4 - wider scraping out from #3)

Sample #5:
collected debris [onto dry cotton swab]
(Vial: #5 - swab to collect fragments)

Sample information recorded by Scott on Margaret's notepad and transcribed by Scott

Samples taken by Margaret Contompasis, 17 July 1996

Spot 2: position 8.6 cm up 1.15 from left edge.

Sample 6:
Dry swab to remove dust; abrasion of surface; 3x3 mm
(Vial: #6 - dry dust Spot 2)

Sample 7:
D.I.[deionized] water swab. Immediate hazing with abrasion of either the surface or the surface deposit.
(Vial:#7 - D.I. water swab of dusted Spot 2)

Vial 8 - only water on swab, not from painting

Sample 8:
2nd D.i. water swab from same spot 2; draggy swab & leaves a streak Right half of spot 2 (1.5x3 mm).
(Vial: #8 - 2nd deionized water on Spot 2)

Sample 9:
3rd D.i. water swab in right half of Spot 2 (1.5x3 mm).
(Vial: #9 - 3rd d.i. swab, it Pt of Spot 2)

Sample information transcribed by Scott from photocopy of notes recorded Ivy Margaret

Samples taken by Scott Williams, 17 July 1996

Sample 10:
slices from rt half 3x's cleaned, seems that varnish is more brittle - fragments shatters rather than slices, reminiscent of plasticizer leaching. Varnish doesn't seem to be less brittle in borders of the cleaned area.
(Vial: #10 - slices from it half thrice cleaned by d.i. water)

Sample 11:
once deionized water swabbed, still freckles visible in traces on the left side - more slicing in sample taken rather than fracture [this is a varnish scraping from left side of spot 2]
(Vial: #11 - once d.i. water swabbed area on left of Spot 2)

Sample 12:
Spot #2 debris cleanup w/ dry swab [from entire area of Spot 2]

(Vial: #12 - Spot 2 debris cleanup, dry swab)

Spot3: 1.3 cm x 12.8 cm

Sample 13:

Flake taken from overlapping paint layer of old damage

(Vial: #13 - Flake)

Sample 14:

Flake, 3 mm up the crack; varnish & particle paint layer.

(Vial: #14 - Flake 3 mm up crack)

Sample 15:

Big flake (SEM). Small portion on it of sample remains soft enough to remain hinged to surface - large portion also hinged a bit.

(Vial: #15 - Big flake (SEM?))

Object: "Beach Scene" by Engel

Spot 1

Sample 16:

(2.6 cm x 49.3 cm LLC) waxy orange substance that flows around needle.

(Vial: 16 - Beach Scene Engel, "waxy" orange between yellow bumps (weave))

Sample 17:

(onto) glass - loose debris from relatively thicker brown area, pretty crumbly, high surface area paint.

Object: "Portrait of Leila in Red" by Harry Engel (1901-1970) (IUAM Acc. No. 71.86.8)

From Accession Card:

oil on canvas, 29³/₄"W x 23³/₄"H

Sample 18:

area of surface coating (slices), synthetic, rubbery, clear, elastic coating, removed square by peeling off surface.

(Vial: 18 - Engel Red Lady "varnish")

Sample 19:

brown paint scraping from area where varnish was peeled off for sample 18; definitely not a brittle film.

(Vial: #19 - Red Lady paint Spot 1 under removed varnish)

Sample 20:

location measurement taken from inside of frame, 20.5 cm x 1.9 cm. very small cross-section - larger section that is v. fragmented and held in place by soft plastic-like surface

coating.

(Vial: #20 - chip from Red Lady)

Sample information recorded in Scott's Labbook p. 45-47 and transcribed by Scott

Object: Plexiglas glazing on Poster "Salon Rose Roix" on IUAM painting storage rack

Samples taken by Margaret Contompasis, 18 July 1996

Area 1 measuring about 5" x 4" at bottom right corner

Sample 21 and 22:

Dry swab fro 5" x 4"; greasy and looks greasy; smeared - greasy film remained.

(Vial: 21 - Dry swab)

(Vial: 22 - Area 1 Poster, more dry)

Sample 23:

D.I. water swab from precleaned area (sample 21 and 22), water beads more than expected on Plexiglas, no greasy film remains (Plexi is polished).

(Vial: 23 - Poster Area 1, d.i. water after dry)

Sample 24:

Dry swab to collect residual water drops from Area 1, remaining after #23, still has slight redistributed, perhaps undissolved, material that has been pushed around [by swab].

(Vial: #24 - Poster Area 1, dry swab to collect beaded water drops)

Area 2 measuring about 4" x 5" taken at bottom right corner, immediately to the left of Area 1

Sample 25:

D.i. water swab: water beads up, but plexi looks polished between beads.

(Vial: 25 - Poster Area 2 d.i. water swab)

Sample 26:

fell on floor: Dry swab to pick up residual water drops, left a smeared greasy film.

(Vial: 26 - Poster Area 2, dry swab after water swab to collect beads, fell onto floor)

Comparing Area 1 with Area 2 indicates that initially dry swab removes material to prevent smearing when subsequent water swabs are used. Wet before dry, with residual droplets from wet, leaves smear after dry.

Area 3: same size from area immediately to left of Area 2

Sample 27:

D.i. water swab; initial droplets follow stroke of swab, [plexi] looks polished between droplets.

(Vial: 27 - Poster Area 3, d.i. water swab)

Sample 28:

dry swabbed dragged over surface to pick up droplets, area allowed to dry, a smeary film results, same dry swab over this results in polished surface with slight residual film.

(Vial: 28 - Area 3 Poster, dry swab after d.i. water swab)

Area 4: area about half the size of previous areas, immediately to left of Area 3

Sample 29:

D.i. water swab - leaves water beaded on surface - allowed water droplets to dry [what happened?]

(Vial: 26 Poster Area 4, d.i. water swab)

Object: "Magdalen Reading" by Master of the Female Half-Lengths (IUAM Acc No. 77.12.1)

Information transcribed from Accession Card (see Labbook, .p. 39):

H20" x W16⁵/₈" x T 1/4":11/16". Construction: Support Vertical-grain hardwood panel, thinned and cradle applied, Ground Thin white, Surface coating. Medium-gloss, medium thick, Paint: Thin oil-type?, Reds glazed, Blue-purple dress w/brown sleeves sunk. Inspection Aug 82: Support: flat appears stable. Too tightly framed 3/8" along left edge is repaint, Repaint sol. xylene. Ground-Paint: Sharply ridged craquelure - no active cleavage Surface-coating: Some matt areas - esp. inpainted parts. Drip marks Care Grime cleaned Wax (Renaissance) applied w/ rayon boll. Watercolor inpainted loss in bodice. Shaved down cork fillers for frame, refrained. 7/21/83: Support: OK: (old). Ground: "[as Aug 82]. Surface coating: In paint matt. Care: Revarnish inpaint? Sept. 9. 1984: Support: several beetle holes in frame. Ground-Paint Watch top left to left of head for testing [tenting?]. Surface coating: dusty and fingerprints, dull areas [...illegible...(on?)] varnish, esp. lower 1/2 below book & below right proper forearm. Care: Surface clean and possibly remove varnish. Feb 2 '93: Support: as above [Sept 9., 1984]. Ground-paint: Surface here is raised but stable. Surface coating: upper bkgnd is badly hazed & white (DEAE?). Care: Needs cleaning. DEAE problem -

Sample information transcribed from Scott's Labbook, pp. 41, 51:

Samples taken 18 July 1996 by Margaret Contompasis

Area 1 - 38.5 cm up, 6.5 cm from left

Sample 30:

Light dry swab for dust - debris moves around, not sticky, swab slides easily, slight bluish haze on surface

(Vial: 30 - Magdalen, dry swab for debris)

Sample 31:

d.i. water swab: no immediate hazing in varnish, water beads, dry to leave spots (freckles), still has bluish surface haze, looks same as after dry swab (not changed by water)

(Vial: 31 - d.i. water)

Area 2 – 36.7 cm up, 7.5 cm from left, Area sampled fills graticule rectangle from 36x24mm film at 12.2X magnification setting on microscope.

Sample 32:

dry swab for particle/dust removal

(Vial: #32 - Magdalen Area 2, dry swab to remove dust)

Sample 33:

dry swab scrubbed to remove filmy deposit, film is removed, maybe slight haze retained.

(Vial: #33 - Magdalen Area 2, dry swab scrubbed to get film)

Sample 34:

water swab over #33. Slight haze forms initially then clears with second pass of same swab.

(Vial: 34 - Magdalen Area 2, water swab after dry swab)

Sample 35:

Varnish slices from water swabbed area of 34

(Vial: 35 - Magdalen varnish slices after water swab)

Sample 36:

Debris [collected] on swab

(Vial: #36 - scraping debris)

Samples taken by Scott Williams, 18 July 1996

Area 3 - 36.3 x 8.3

Sample 37:

Scraping, not prior treatment, doesn't seem to be as brittle as pre-treated area - does wet treatment extract plasticizer or does material on the surface hold the sliced surface coating in place?

[Brittleness is judged by how easily fragments pop off surface or are "tiddly-winked" away from working area - more brittle stuff more likely to tiddly-wink away, unless fragments are held together by some sort of consolidating deposit on surface, e.g. grease]

(Vial: #37 - Magdalen, Area 3, varnish slice)

Sample 38:

paint from underneath scraped varnish in Area 3

(Vial: sample 38 - paint sample from under varnish in Area 3)

Object: DEAE boiler treatment products from Margaret Contompasis

Sample 39:

DEAE 1:

Neutralizing Amines [...illegible number (?260449326?)]

Diethylaminoethanol

Morpholine

Sample 40:
DEAE 2:
Surtech Corporation
P.O. Box 90406
Indianapolis, IN 46290-0406
(317) 254-9483
1 pint B-0002

Additional samples and experimental materials were supplied by Margaret Contompasis.

Fragments of paintings exposed at Lilly Library

two fragments of paintings which were placed in ventilation inlet grate in room of Lilly Library; installed Mar 1995, removed about 3 months later.

“Blue Sky”

Sample 41:
painting fragment measuring 77 mm x 73 mm, with glass microscope slide taped to one long edge; oil? on canvas

Sample 53:
scraping of area of 3mm x 4mm, weighing 0.5mg

Sample 55:
water swab from area 16mm x 13mm

“Green Tree”

Sample 42:
painting fragment measuring 59 mm x 77 mm, with glass microscope slide glued to one long edge, unknown medium on canvas, has thick “varnish” may be glue.

Sample 54:
scraping of area of 4mm x 5mm, weighing 0.7mg

Sample 56:
water swab from area 12mm x 13mm

Fragment of “Horses” - Research Painting #3

Sample 43:
rectangular painting fragment measuring 146 mm x 50 mm, greyish, oil? on canvas

Fragment of “Sea Scape” - Research Painting #5

Sample 44:

rectangular painting fragment measuring 115 mm x 56 mm, pale blue, unknown medium on matt board.

Cleaning swabs from Madame Chinnery 6/95

Sample 45:

ziploc bag of about 40 swabs with yellow and grey discoloration
These have been analyzed by Greg Barrett-Wilt, but I have no data.

Sample 64:

methanol extract of three swabs

Powder from “de Ring”

Sample 46:

sample is between two glass microscope slides, labelled “de Ring”

Plexi strip dated 11/9/87

Sample 47:

colorless acrylic sheet measuring 99mm x 433mm with greasy or hazy film on both sides.
Labeled: “11/9/87”

sample 57:

methanol swab from area 35mm x 35mm on labelled side of sheet

Sample 58:

methanol swab from area 35mm x 35mm on unlabelled side of sheet

Stuart Davis back

Sample 48:

plastic ziploc bag with several large cotton swabs, look moldy
labelled: “Mylar on back of Swing Landscape Stuart Davis”

Sample 59:

methanol extract of one swab

E. DeWitte “Interior”

Sample 49:

plastic ziploc bag with about 20 swabs with slight yellowish stain
labeled: “de Wine/Interior of Church”

Sample 60:

methanol extract of one swab

Terborch “Portrait of a Lady”

Sample 50:

plastic ziploc bag with about 15 swabs with yellow-grey stain
labelled: “Terborch Portrait of a Woman”

Sample 61:

methanol extract of one swab

Soulages back, dry sample

Sample 51:

plastic ziploc bag with greyish brown granular powder
labelled: “Soulages Peinture 70.86”

Sample 62:

methanol extract of 1.1mg powder

Balthus back, dry sample

Sample 52:

plastic ziploc bag with greyish brown granular powder
labelled: “Baithus, La Fenetre 70.62”

Sample 63:

methanol extract of powder

B-1

Appendix B				
Results of Thermal Desorption/Gas Chromatography/Mass Spectrometry (u:\deae\deaeprg2.wk4)				
DEAE/methanol solutions, 5 microL injected				
Filename	DEAE conc (ppm) Sample description	deae rt0	peak height	DEAE Present
sw127	meoh	none	0	no
sw129	no inj	none	0	no
sw131	meoh	8.13	1500	no
sw133	meoh	7.929	2000	no
sw178	meoh	none	none	no
sw182	cotton swab meoh extract	7.75-8.1	none	no
0 ppm			1750	
sw156	10	7.8	2500	no
sw179	10	7.75	3200	no
10 ppm			2850	
sw128	16	7.255	4000	no
sw123	16	7.955	7500	no
sw55	16	7.647	12000	no
sw56	16	7.6	13000	no
sw126	16	7.685	17000	present
sw79	16	7.693	19000	present
sw54	16	7.698	40000	maybe
sw53	16	7.546	50000	maybe
16 ppm			20313	
sw160	50	0.601	21000	present
sw157	50	7.586	26000	present
sw164	50	7.619	34000	present
sw166	50	7.535	50000	present
sw180	50	7.55	17000	present
50 ppm			29600	
sw144	100	7.6	55000	present
sw134	100	7.501	80000	present
sw130	100	7.526	80000	present
sw181	100	7.6	36000	present
100 ppm			62750	
sw48	800	7.296	1400000	present
sw78	800	7.447	1500000	present
sw47	800	7.262	2100000	present
sw125	800	7.299	2400000	present
sw50	800	7.275	5500000	present
sw52	800	7.248	6000000	present
sw51	800	7.246	6200000	present
800 ppm			3585714	
sw132	1000	7.295	1900000	present
1000 ppm			1900000	
Ste.Catherine, methanol extract, 5 microL injected				
Filename	DEAE conc (ppm)	deae	peak	DEAE

B-2

	Sample description	rt0	height	Present
sw95	#1cath1drydust	7.83-8.1	2000	no
sw135	#1cath1drydust	none	none	no
sw96	#2cath1dryswab	8.001	1500	no
sw136	#2cath1dryswab	none	none	no
sw137	#4cath1scrape	none	none	no
sw139	#5cath1vam	none	none	no
sw140	#6cath2drydust	none	none	no
sw145	#7cath2waterswab	none	none	no
sw143	#8cath2waterswab2	none	none	no
sw142	#9cath2waterswab3	none	none	no
sw171	#10cath2slicesvam	none	none	no
sw172	#11cath2scrape 1wash	none	none	no
sw149	#12cath2debris	none	none	no
sw162	#13cath3flake	7.92	4000	no
Beach Scene by Engel				
Filename	DEAE conc (ppm) Sample description	deae rt0	peak height	DEAE Present
sw161	#16 orange scrape	7 8-8	0	no
Glazing from "Salon Rose Roix", methanol extract, 5 microL injected				
Filename	DEAE conc (ppm) Sample description	deae rt0	peak height	DEAE Present
sw111	#21postdry1	7.62	6000	no
sw110	#22postdry1	7.66	6000	no
sw146	#23postwat1	7.572	27000	present
sw112	#24postdry1	7.805	2000	no
sw113	#25postwat2	7 518	40000	present
sw115	#27postwat3	7.62	9000	no
sw150	#27postwat3	7.905	1800	no
sw151	#27postwat3	7.68	4900	no
sw147	#28postdry3	7.73	4000	no
sw148	#28postdry3	7.88	3200	no
sw167	#29postwat4	7.673	9500	maybe
Magdalen Reading, methanol extract, 5 microL injected				
Filename	DEAE conc (ppm) Sample description	deae rt0	peak height	DEAE Present
sw169	#30. dry swab, debris	none	0	no
sw158	#31. water swab	7.803	3000	no
sw159	#32. dry swab, dust	7.804	2500	no
sw170	#33. dry swab, area 2	none	none	no
sw163	#34. water swab	noise	noise	no
sw173	#36. scraping debris	none	none	no
sw174	#36. scraping debris	none	none	no
Paintings exposed at Lilly Library (which still uses DEAE), methanol extract of scraping				

Filename	DEAE conc (ppm) Sample description	deae rt0	peak height	DEAE Present
"Blue Sky"				
sw153	#53. 0.5mg scrape(3x4)	none	0	no
sw184	#55 water swab(16x13)	none	none	no
"Green Trees"				
sw154	#54. 0.7mg scrape(4x5)	none	0	no
sw185	#56. water swab(12x13)	none	none	no
Acrylic strip dated 11/9/87				
Filename	DEAE conc (ppm) Sample description	deae rt0	peak height	DEAE Present
sw175	#57. labelled side water swab(35x35)	none	none	no
sw176	#58. unlabelled side water swab(35x35)	none	none	no
Other IUAM swabs from paintings (some analyzed by Greg Barrett-Wilt (prefixed by GABW and GBW))				
Filename	DEAE conc (ppm) Sample description	deae rt0	peak height	DEAE Present
sw116	#61 Terborch "Portrait of a Lady", swab	none	0	no
sw117	#60. De Witte "Interior of Church", swab	none	0	no
sw118	methanol	7.15	1100	maybe
sw119	#59 Stuart Davis "Swing Landscape", swab	7.986	1300	maybe
gbw0008	S.18 "Stuart Davis #2 surf. dirt" second cleaning	7.3	34000	(present)
gbw054	StuDav back 5-6 large swab, 30 Nov 96	13.6	600000	(present)
sw120	#63 Balthus "La Fenetre", powder	none	0	no
gabw0008	Balthus, powder, 4 Apr 96	14.8	4000	(no)
sw121	#62. Soulages "Peinture", powder	7.88-8.1	2500	maybe
gabw0009	Soulage "Peinture", powder	14.2	480000	(present)
Chinnery, methanol extract of cleaning swab, 5 microL injected				
Filename	DEAE conc (ppm) Sample description	deae rt0	peak height	DEAE Present
sw31	#64. Chinnery	none	0	no
sw58	#64. Chinnery	7.495	25000	probably
sw59	#64. Chinnery	7.548	13000	probably
sw60	#64. Chinnery	7.74	3300	maybe
sw61	#64. Chinnery	7.446	40000	present
sw 83	#64. Chinnery	7.588	27526	present

Appendix C: Results of FTIR spectroscopic analysis

The following table summarizes the data from the IR spectra. Table entries have the following format. Each spectrum is identified by a number of the form 693.3b2 where 693.3 indicates the spectrum is from Sample 3 taken from the paintings. In most cases only part of the entire sample taken from the painting was selected for each spectrum. Usually this was one of several fragments of a scraping taken during sampling or a single layer or colored particle from a paint chip. The “b” indicates that the spectrum is for the second particle or aliquot of Sample 3. The final “2” indicates that the spectrum is from a reaction product of the sample, usually obtained by adding reagents to the specimen while it is on the diamond cell used to hold the specimen in the spectrometer, as described on page 9 of the report. Thus spectrum 693.3b2 is the second reaction product of the second particle from painting sample 3.

For each spectrum a list of wavenumbers for the absorption bands is given with an assignment of the chemical bonds responsible for the band. Not all bands are listed, only those that are key in determining the composition of the sample. In some cases bands are listed without an assignment, where the absorption is due to unknown chemical bonds.

Finally, for each sample, a summary is given to describe the chemical composition of that sample as determined by interpretation of its spectra.

Abbreviations: s: strong, w: weak, sh: shoulder, sp: spike (very sharp narrow, usually not strong peak)

“Ste Catherine”

693.3a (Sample 3 - Area 1, chip of varnish after two dry swabbings):

3400-3500: hydroxyl

1700: acid but no ester at 1735 (varnish resin acids)

1457/1374: CH

1242: ?

1030: may be starch or similar carbohydrate

693.3a1 (693.3a + DEAE: most dissolved with tiny bit of gelatinous stuff left):

1735: 1700 (acid) shifts to 1735 (ester)

1237: shifted from 1240 but relatively unchanged

1030 (starch?): unaffected

1456 disappears but 1374 unaffected,

693.3a2 (693.3a + DEAE + WATER)

spectrum unchanged by addition of water to DEAE reaction product

693.3a “Ste Catherine” Summary: Resin varnish such as dammar + carbohydrate such as starch + unknown (1242). Resin acids (1700) react with DEAE to give esters (1735). No esters were present in original spectrum so no significant reaction occurred between varnish and DEAE in gallery.

693.3b (Another particle from Sample 3)

3408: hydroxyl

3000: lots of Ch, no C=C at 3030

1706: acid

1720: sh: weak ester?

1457/1377: Ch like resin

1241:?

1160sh/1115w/1030s: starch is 1160w/1080w/1030s

Note: very similar to 693.3a

693.3b1 (693 3b + DEAE)

1734: shifted from to 1706, ester produced by reaction of DEAE with acids

1457 greatly diminished

1372: shifted from 1377 but relatively unchanged

1237: shifted from 1241 but relatively unchanged

1160/1115 disappears, 1030 shifts to 1035 but still strong

Note: very similar to 693.3a1

693.3b2 (693.3b + DEAE + water)

1239: shifted from 1242 and greatly reduced

Note: 1242 much more reduced here than in 693.3a2

693.3b “Ste. Catherine” Summary: very similar composition and behaviour a 693 3a, except for reduction of 1242 by water.

693.10a (Sample 10 - Area 2, varnish after three water swabbings)**693.10b** (Another particle from Sample 10)**693.11a** (Sample 11 - Area 2, varnish one water swabbing)**693.11b** (Another particle from Sample 11)

693.10/11 “Ste Catherine” Summary: These spectra are very similar to aged dammar (CCI Damar 1948) with no carbohydrate or protein adulteration. Is it possible that there is no carbohydrate present because the water swabbing removed these water soluble components?

693.13a (Sample 13 - Area 3, brown paint taken before swabbing):

3407: hydroxyl

3000-2800: lots of CH

1708: acids but no ester at 1730 (like resin)

1652/1535: this pair indicates protein like glue

1447/1413/1390: carbonate (plus CH?)

882: calcium carbonate

837: lead hydroxy carbonate

1242: ?

1166/1106/1074/1030: barium sulfate + starch

693.13a1 (693.13 + HCl/MeOH)

3407 splits into two broad bands at 3390 (shifted 3407?) and 3196 (new?)

1707: acid, unaffected
 1652/1535: protein disappears
 1453 wk + 1403 wk: most of 1447-1390 due to carbonate is removed by HCl
 1242: ?, unaffected
 1163/1135/1075/1059/1034: sulfate plus starch relatively weaker than in previous treatment

693.13a2 (693.13 + HCl/MeOH + DEAE)

3390/3190 doublets joins to 3366, originally about 3407
 1736: ester formed and negligible acid (1707) remains
 1655/1567: protein reappears
 1242: ?, unaffected
 1163/1135/1075/1059/1034: sulfate plus starch, relatively strong

693.13a3 (693.13 + HCl/MeOH + DEAE + HCl)

1733 ester decreases, 1712 acid increases (but not as strong as originally)
 1650/1560 protein disappears again
 1400: nothing, all carbonate removed
 Note: This now looks very similar to resin plus barium sulfate plus starch + 1238

693.13 “Ste. Catherine” Summary: Resin acids indicating varnish + lead and calcium carbonates + protein + carbohydrate. Seems to be pigmented varnish, not an oil paint (no ester, thus no oil). Resin acids are converted to ester by reaction with DEAE as in 693.3. No esters were present in original sample spectrum, indicating that there was no reaction with DEAE in gallery. Protein and starch are water sensitive materials. The acids are not fatty acids produced by hydrolysis of oil by DEAE because these acids would react with calcium and lead carbonates to produce calcium and lead carboxylate salts, which were not observed (no bands at 1490-1500 for lead carboxylate or 1540-45/1575-80 for calcium carboxylate).

“Magdalen Reading”

693.37a (Sample 37 - Area 3: scraping of varnish prior to any water swabbing)

about 3400: hydroxyl
 2924/2854, 1449, 1375: relatively strong peaks, indicating lots of aliphatic CH
 1706: organic acid but not ester, typical peak for resin varnishes
 1250, 1169, 1052: C-O-C and C-O-H bonds of alcohols, ethers and carboxylic acids
 1050: stronger than usual and lower wavenumber than for resin acids, but ok for carbohydrates and primarily alcohols

693.35a (Sample 35 - Area 2: varnish slices from area of sample 34 after water swabbed):
 indistinguishable from 693.37a

693.35/37 “Magdalen Reading” Summary: Resin like dammar + carbohydrate like starch. Very little difference between unswabbed and water swabbed samples, indicating that carbohydrate not soluble in water, or not accessible to water (i.e., bound up in resin). Cannot say whether carbohydrate is separate phase from resin.

693.38a (Sample 38 - paint from underneath scraped varnish in Area 3)

3407: hydroxyl

1734: ester

about 1650 sh: maybe protein, but not likely since companion 1550 not present

1451, 1379, 1264, 1130, 1070, 778, 743: typical pattern (fingerprint) for ortho-phthalate alkyd

(cf "Medium oil alkyd Desoto Alkyd #19, Coatings Atlas #37), i.e. , alkyd paint and definitely not drying oil.

693.38b (another particle from #38 sample with a more distinct pale red color)

very similar to 693.38a

contains all alkyd peaks, plus some others

1650: distinct peak, rather than shoulder. May be amide but since no peak at 1560, not

likely protein (glue)

weak, sharp peaks at 1412, 1320: may be due to red organic pigments which often contain many relatively

weak sharp peaks in this region. (Note. DEAE has two of its strongest peaks at 1461 and 1381 (slightly stronger), nothing at 1320, and strongest peaks at 1050 so DEAE is not likely source for this peaks).

693.38c (another spot on 693.38b, more opaque, less red)

very similar to 693.38b, but peaks tentatively attributed to red pigment (1412 and 1320) are less intense, which is in accord with the less intense red color of the sample. 1650 is also less intense, and is perhaps from red colorant.

693.38 "Magdalen Reading" Summary: medium oil o-phthalate alkyd + red organic colorant.

"Modern" paint, probably and inpaint.

"Beach Scene"**693.16a, 693.16b:** (Sample 16 - waxy orange substance that flows around needle when sampling)

2918, 2849, 1540, 1458, 1398, 745, 722: very characteristic pattern for zinc carboxylate salt like zinc stearate

1738: ester (relatively weak component), possibly oil

1593: ?

1320: ?

1168, 1100, 1060 sh, 982sp, 884, 819: ?

693.16a1 (693.16a + DEAE, DRIED: paint fragment disintegrated immediately upon addition of DEAE, and particles moved about in the DEAE driven by the turbulence due to evaporation of the DEAE.

1738: ester, unchanged

1591: increased (reaction product?) and 1540 much reduced

1460 and 1408 (shifted from 1398): much reduced

Note relative intensities of 1460, 1408, 1540 in this spectrum are similar to relative intensities of 1540, 1458, and 1398 in 693.16a, indicating that zinc carboxylate still present but much reduced by conversion to 1591 product.

1320: ?, unchanged

1168/1100: disappears, probably because they are from a component that is soluble in DEAE
 1060, 982: DEAE dissolves/disperses components that absorbed at 1168/1100 leaving the
 1060/982. The relative strengths of 1060 compared to 982 in the original and in the DEAE
 treated material look quite similar indicating that they are common to a single component in
 the paint.

822: shifted from 819

693.16a2 (693.16a + DEAE + HCL):

1708: acid

1735 w, sh: very weak ester

1591: disappeared

Acid (1708) is produced by conversion of 1540 (carboxylate salt) and maybe some 1738
 (ester)

1320: disappeared

1060/982: unchanged by HCl treatment (pigment or filler)

822: disappears

693.16 “Beach Scene” Summary: Predominantly zinc carboxylate salt + small amount of ester (oil) +
 inorganic pigment. Much material dissolves when sample flooded by DEAE Some zinc carboxylate reacts
 with DEAE to form product at 1592. Some 1592 present in original spectrum therefore may have been some
 reaction of paint with DEAE in gallery.

693.17 (Sample 17 - loose debris from relatively thicker (compared to sample 16) brown
 area, pretty crumbly, high surface area paint.)

2914, 2864, 1540, 1457, 1397, 948 (not in 693.16a), 742, 714: zinc carboxylate (as in
 693.16a)

882: also in 693.16a

1168, 1100: also in 693.16a

1060/982 which were present in 693.16a (orange) are not present in this sample (brown).

693.17 “Beach Scene” Summary: predominantly zinc carboxylate salt, very similar to
 693.16a

“Portrait of Leila in Red” by Harry Engel

693.18a (Sample 18 - surface coating, synthetic, rubbery, clear, elastic coating; removed
 square by peeling off surface)

spectrum matches poly(n-butyl methacrylate)

693.18a1 (693.18a + DEAE)

varnish dissolved and redeposited

spectrum of deposit identical to 693.18a

693.18 “Leila” Summary: Varnish is poly(n-butyl methacrylate). It is soluble in DEAE, but does not react
 with DEAE.

693.19a (Sample 19 - brown paint scraping from area where varnish was peeled off sample)

18; definitely not a brittle film)

1735/1711: mixture of carboxylic esters and acids (perhaps oil+ resin, no apparent contamination of spectrum by methacrylate varnish)

1636, 1547: protein (glue or egg?)

1537 w: may be zinc carboxylate as seen in "Beach Scene")

2928, 2855, 1465, 1364: CH from carboxylic acids and esters

1410, 1320: ?

1182, 1115, 1073, 984: barium sulfate

913: ?

798: ?

693.19a1 (693. 19a + DEAE)

1632: unchanged

1592 appears and 1537 disappears: reaction product of zinc carboxylate and DEAE as observed in "Beach Scene"

Disappearance of 1547 but not 1632 suggests that these are not due to protein, otherwise both would have disappeared.

1460, 1402, 1320: become more prominent [The same happens in 693.16 "Beach Scene"

1185, 1116, 1075, 984: barium sulfate is unchanged

693.19a2 (693.19a + DEAE + HCl)

1709: carboxylic acid.

1650: shifted from 1632

1592: completely disappeared, (converted to 1709 acid, ie 1592 is a reaction product that exists in neutral to alkaline conditions, but reverts to acid in acid condition, ie a DEAE/carboxylate salt)

1462, 1399: slight shifts

1320: disappears

1185, 1116, 1074, 984: barium sulfate is unchanged

The appearance of 1592 after DEAE treatment of "Beach Scene" paint (zinc carboxylate with some ester) was noted. Perhaps this is a reaction product of DEAE and carboxylic esters or acids.

693.19 "Leila" Summary: Ester (oil) + acid (resin acid or oil acids) + zinc carboxylate salts + barium sulfate + perhaps protein.

"Blue Sky" (unvarnished, oil? on canvas)

693.54a and **693.54b** (surface scraping of paint same as used for gc)

1740: ester (as in drying oil), not acid (1710)

1587: "DEAE/ester reaction product" or aluminum carboxylate?

1418: carbonate (lead or calcium)

1319: ?

1184/1118/1080/986: barium sulfate

693.54b1 (693.54b + DEAE, DRIED + DEAE, DRIED)

spectrum unchanged from 693.54b

693.54b2 (693.54b + DEAE, DRIED + DEAE, DRIED + HCL, DRIED)

1740: ester, unchanged

1711 (acid) appears and 1587 disappears: DEAE or Al carboxylate + HCl = acid

1462/1377: CH of carboxylic acid

1418: carbonate decomposed

1183/1117/11077/983: barium sulfate unchanged

693.54b3 (693.54b + DEAE + HCL + DEAE)

poor spectrum, difficult to interpret with confidence

1735: carboxylic acid converted to carboxylic ester

1612 broad: DEAE/acid reaction product?

barium sulfate unchanged

693.54 “Blue Sky” Summary: Oil + barium sulfate + 1587 which may be DEAE

carboxylate formed by reaction of DEAE with fatty acids from hydrolyzed oil esters or

aluminum carboxylate, an additive. Zinc carboxylate + DEAE yields a compound with a broad absorption at 1592 (see “Beach Scene” above).

“Green Trees” (unknown medium on canvas, has thick “varnish” may be glue)

693.42a (clear brown chunk picked out of varnish layer)

very similar to “Dammar March 1948”, a film of dammar varnish cast on glass in 1948;

definitely not glue. The spectrum has a broad strong band at 1716 perhaps with a shoulder at around 1550-1600 (DEAE/acid reaction product?)

693.42a1 (varnish + deae, dissolved, dried in air + dried under microscope lamp)

1707 remains but very much reduced

1572: strong new peak, also in reference dammar + DEAE

1457/1387: relatively unchanged (re untreated sample)

1239/1180: disappear

1300-1133: several small peaks

1082/1040 doublet appears, not DEAE which has dominant peak at 1052

693.42a2 (same air dried overnight)

contains all the same peaks with the exception that 1293 has disappeared and 1084/1036 is weaker

693.42a3 (VARNISH + DEAE + HCL)

spectrum is nearly identical to untreated varnish with exception that weak 1078/1030 doublet is now present (remains from DEAE treatment)

693.42a “Green Trees” Summary: Varnish is dammar. When reacted with DEAE band at

1578 is formed and 1710 (acid) is decreased. This is not an ester, thus reaction of DEAE with resin acids is not esterification with alcohol group of DEAE, but rather carboxylate salt formation by reaction with nitrogen of DEAE, analogous to ammonium carboxylate salts. A

slight broadening of the 1716 band at 1550-1600 in the original spectrum may be DEAE/resin reaction product indicating that some reaction has occurred between varnish and DEAE in gallery.

693.42b (varnish from spot scrubbed by two water swabs)

Very nearly identical to varnish from untreated spot, with the possible exception that a shoulder at 1550-1600 which seems to be in the untreated varnish does not appear to be in the water swabbed varnish. This band is tentatively attributed to a DEAE/resin acid or ester reaction product. This may be water soluble and has been removed by water swabbing.

Powder from “de Ring”

693.46a (powdery material between two glass slides, labelled “de Ring”)

The spectrum matches a copolymer of vinyl acetate with a few percent of ethylene (less than 5 % ethylene).