**US Department of the Interior**
**National Park Service**
**National Center for**
**Preservation Technology and Training**
**Publication No. 1998-17**

# Analyzing the effect of diethylaminoethanol, an indoor air pollutant, on traditional easel paintings Phase 2

**IUAM DEAE* Analysis Project Final Report for Phase 2:**
**Infrared Spectroscopic Analysis of Varnish and Paint Samples**
**From IUAM Paintings for the presence of DEAE**
**(*DEAE: diethylaminoethanol)**

**by**
**R. Scott Williams**
**Conservation Scientist (Chemist)**
**Conservation Processes and Materials Research**
**Canadian Conservation Institute**

**for**
**Margaret Contompasis,**
**Painting Conservator, IUAM**

**May 31, 1997**

Funding for this report was provided by the National Park Service's National Center for Preservation Technology and Training. NCPTT promotes and enhances the preservation of prehistoric and historic resources in the United States for present and future generations through the advancement and dissemination of preservation technology and training.

NCPTT's Preservation Technology and Training Grants program develops partners in non-profit organizations, universities and government agencies throughout the United States to complete critical research, training, and information management work, and lends significant support to developments in the conservation and preservation community.

This publication was developed with finds from the Preservation Technology and Training Grants program. Its contents are solely the responsibility of the author and do not necessarily represent the official position or policies of the National Park Service or the National Center for Preservation Technology and Training.

## IUAM DEAE Analysis Project

### Final Report for Phase 2:
### Infrared spectroscopic analysis of varnish and paint samples from IUAM paintings for the presence of DEAE

### CCI Service Request No. CPMR 693

## Table of Contents

# IUAM DEAE Analysis Project

# Final Report for Phase 2:
# Infrared spectroscopic analysis of varnish and paint samples from IUAM paintings for the presence of DEAE

### CCI Service Request No. CPMR 693


### Summary

FTIR analysis was performed on 74 samples from 21 paintings from IUAM. Most painting samples has several components or layers, and all were analyzed. More than 500 spectra were collected for these components, and interpreted to identify the chemical composition of these components.

Model compounds to represent the major organic components of paintings were exposed to various concentrations of DEAE and the products of reaction were analyzed.

Studies on the model compounds showed that DEAE can react with the acidic components of paintings, in particular with the resin acids in natural resin varnishes, and free fatty carboxylic acid in drying oils. However, DEAE does not react with carboxylic esters of glycerol, and therefore is unlikely to react with the triglyceride esters that comprise the major component of drying oils.

DEAE reaction products, specifically DEAE carboxylate soap, was tentatively identified in only one painting, “Peinture” by Soulages. It was found in the ground layer, but in no other layers, including an acidic oil layer on the surface, where the potential for reaction is greatest.

Small amounts of oxalate compounds, perhaps calcium oxalate, were detected in several paintings. One source of oxalic acid and its salts is metabolic by products from molds, fungus, and algae.

The analyses reported here indicate that the IUAM paintings have not been damaged by reaction with DEAE.

# IUAM DEAE Analysis Project

# Final Report for Phase 2:
# Infrared spectroscopic analysis of varnish and paint samples from IUAM paintings for the presence of DEAE

### CCI Service Request No. CPMR 693

## 1. Introduction

This Final Report on Phase 2 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 2 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 "Final Report for Phase 1, Revision 1" was delivered to IUAM on January 15, 1997. The analyses in Phase 1 indicated that DEAE and its reaction products are present on some paintings, but that 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 in Phase 1 was so small it was recommended that more paintings be analysed to get a true picture of the extent of the DEAE contamination problem.

The specific recommendations were:

> 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 analysed 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.

The results of work performed by CCI to address these recommendations are given in this Final Report for Phase 2. CCI has delivered four Progress Reports on Phase 2 activities on March 21(20 samples), March 21 (6 samples), May 6 (12 samples), and May 7 (9 samples). This Final Report for Phase 2 incorporates, and supersedes, these previous Progress Reports.

## 2. Methods of Analysis

### Fourier transform infrared (FUR) microspectroscopy

All samples were analysed by Fourier transform infrared (FTIR) microspectroscopy in the spectral region of 4000 to 700 $cm^{-1}$ by mounting samples in a diamond cell sampling accessory in a Spectra-Tech IR Plan microscope interfaced to a Bomem MB-120 FTIR spectrometer. The spectrometer is controlled and data is manipulated by GRAMS-386 software from Galactic Industries running on a Pentium 133 computer. This method is described more fully in Section 4.2 of the Final Report for Phase 1.

The composition of each component of each sample was determined by interpretation of their IR spectra. This process consists basically of assigning every IR absorption (i.e., every peak) in the IR spectrum to a chemical compound, by comparing the sample spectrum to spectra of reference materials. Every compound has an IR spectrum consisting of absorptions (peaks) at various wavenumbers and of varying intensities that produces a pattern that can be used as a fingerprint to reveal the presence of the compound in a sample. A compound is present in a sample only if all the absorptions of the compound are present in the sample spectrum. Only compounds absorbing at 4000-700 $cm^{-1}$ are detected.

## 3. Samples and Sample preparation

### IUAM painting samples

Painting samples for analysis in Phase 2 were provided by Margaret Contompasis from the following IUAM paintings.

“Peinture” by Soulages (IUAM Acc. No. 70.86)
“Portrait” by Artist Unknown, Style of Biedermeyer (IUAM Acc. No. 96.25)
“In Staccato” by Pearle Fine (IUAM Acc. No. 79.73)
“After Picasso Woman Looking in Mirror” by Harry Engel (IUAM Acc. No. 14)
“Magdalene at her Toilete” by Gentilesci (IUAM Acc. No. 66.113)
Etty (IUAM Acc. No. 57.34)
“Ste. Catherine” by Zagnelli (IUAM Acc. No. 77.43)
“Landscape” by Valtat (IUAM Acc. No. 73.14.3)
de Pazzi (IUAM Acc. No. 71.101)
“Arctic Scene” by Bradford (IUAM Acc. No. 68.218)
Andrea del Sarto (IUAM Acc. No. 79.101)
Thos Hart Benton Murals
IUAM Acc. No. 78.67.1

IUAM Acc. No. 78.62.2
“#11” by Jackson Pollock (IUAM Acc. No. 75.87)
BRW1, from Lilly Library
A1072, from Lilly Library
LRM1, from Lilly Library
WCB, from Lilly Library
R2664, from Lilly Library

The samples are listed in Appendix A along with sample locations and descriptions provided by Margaret Contompasis.

Painting samples were received in vials or on microscope well slides covered by another microscope slide. In general, samples consisted of more than one particle, usually with each particle containing more than one component. A painting sample can consist of strata of varnish, paint, priming, ground, and support. Each of these strata can have several layers. Also, the painting sample may have accretions or additional materials from treatments such as adhesives, overpaints, and new varnish. Each layer in a stratum, accretion, or additional material is a component. For this project I attempted to separate and isolate each component observed in the sample (i.e., each layer or accretion), in order to get IR spectra of every component. Separations were achieved by slicing with scalpels, poking with needles, and crushing between microscope slides to cleave between layers, all while observing the sample with a stereomicroscope.

**Model compounds to simulate painting components**

To investigate the reactions that might occur in paintings exposed to DEAE in a gallery, the reaction of DEAE with simple model compounds that represent or simulate the key components in real paintings were studied.

The selected model compounds are:

Dammar film cast in 1948
Linseed stand oil cast in 1983
Myristic, palmitic, and stearic acid
Tripalmitin (glycerol tripalmitate), tristearin (glycerol tristearate)
Trilinolenin (glycerol trilinolenate)
Methyl stearate
Aluminum, calcium, sodium, and zinc stearate
Morpholine
Ammonia

They are described more fully in Appendix B along with the reasons for their selection.

## 4. Procedure for reaction of model compounds with DEAE

Model compounds were reacted with DEAE by two procedures - in the diamond cell by direct addition of DEAE liquid or vapor to the model compound on the diamond, and by incubation of model compounds and painting fragments in atmospheres containing various concentrations of DEAE.

**Reactions on the diamond cell**

For DEAE reactions directly on the diamond cell, a particle of the model compound is placed in the diamond cell and a spectrum of the model compound is obtained, then vapors of DEAE are reacted with the sample still on the diamond. DEAE vapor is introduced by bringing a drop of DEAE hanging from a needle close to the sample while observing with a stereomicroscope. The heat of the illumination lamps slowly vaporizes the DEAE which then condenses on the surface of diamond cell and the sample contained thereon, until the sample becomes wet or its dissolved. This reaction product is dried under the lamps, then a spectrum is acquired. This process assures that the reaction product analysed is from the exact sample that was originally analysed. In fact, because a mechanical stage is used to position the sample in the IR microscope for analysis, the exact 100 micrometer circular portion of the sample is reanalysed after reaction with DEAE. This is very useful when analysing specific spots on samples that present various zones in the diamond cell (e.g., different layers, different pigment particles within a layer).

**Incubation of model compounds and painting fragments in DEAE atmosphere**

Painting fragments, scrapings of painting layers, dammar and copal scrapings, and model compounds were placed on glass microscope slides which were then incubated in a closed 9.7L desiccator at room temperature containing DEAE vapors at concentrations of 10000 ppm (1%, 0.1202 g DEAE) and 400 ppm (0.04%, 0.0043 g DEAE) w/w DEAE in air for 3 and 4 days.

## 5. Results of FTIR spectroscopic analysis

FTIR analysis was performed on 14 samples in Phase 1 and 60 samples in Phase 2, for a total of 74 samples, with most containing several components. More than 600 spectra were collected and interpreted. I estimate that about 90% of these are from IUAM painting samples, and the others are from reference materials, model compounds, and reaction products associated with the project.

Copies of all spectra obtained are attached in Appendices E, F, and G. All spectra are stored as computer files in GRAMS-386 format. This can be supplied on diskette, if required.

The detailed results of the FTIR analysis of the IUAM painting samples are given in Appendix C. A summary of results is given here.

The detailed results of the FTIR analysis of reaction products of model compounds with

DEAE are given in Appendix D. A summary of results is given here.

**Summary of results of FTIR analysis of IUAM painting samples**

**"Peinture" by Soulages (IUAM Acc. No. 70.86) (Samples 693.65 to .69)**

White ground under grey paint contains predominantly lead white, some calcium carbonate, a small amount of zinc soap and oil. **Spectra of this layer have absorptions at 1567 which could be DEAE soap (DEAE plus fatty carboxylic acid).**

Grey paint on white ground contains predominantly lead white, bone black, a trace of zinc soap, and oil.

Red material in the grey paint contains silica or silicates and is probably iron earth pigment (iron oxide plus silica or silicates).

A black paint on the white ground contains bone black in oil.

Clear brownish glaze or paint over white ground is oil with free acid. No soaps are present, but treatment with DEAE produces DEAE soap, which is converted back to the original material by addition of hydrochloric acid.

White spheres on the painting surface were not identified. Their spectra are unlike any painting material that I have encountered. They are not soluble in water.

Spectra of some samples contain weak peaks at 1615-1625 and 1315-1321, which may be from calcium oxalate or other oxalates. Oxalic acid and its salts are metabolic by products of molds, fungus, and algae.

The ground may contain DEAE soap, but no other layer contains DEAE or DEAE reaction products.

**"Portrait" by Unknown, Germany, Style of Biedermeyer, (IUAM Acc. No. 96.25) (Samples 693.70 to.74)**

Varnish contains natural resin, perhaps with small amount of oil (which may be from underlying oil paint layers), and traces of protein.

Some scrapings of varnish contained starch. This appears to be from a layer under the varnish and on paint.

Several particles of the varnish scrapings contain pigments, presumably from underlying colored paint layers or glaze layers. Pigments and fillers detected include barium sulfate, calcium carbonate, Prussian blue, iron earth such as sienna (mixture of iron oxides and silicates).

Spectra of some samples contain weak peaks at 1615-1625 and 1315-1321, which may be from calcium oxalate or other oxalates. Oxalic acid and its salts are metabolic by products of molds, fungus, and algae.

No DEAE or DEAE reaction products were found in samples from this painting.

**"In Staccato" by Pearle Fine (IUAM Acc. No. 79.73) (Samples 693.75 to .77)**

Bluish or greyish paint on yellowish ground contains predominantly aluminum carboxylate soap with small amount of zinc carboxylates soap (most likely zinc and aluminum stearates), and oil. This medium would be expected to have very little binding power, so that the paint would be susceptible to abrasion, such as when using swabs for cleaning. Also, although zinc and aluminum soap are not soluble in water, they may swell or soften more readily than a fully crosslinked drying oil film, and may appear to be soluble, or sensitive, to water moistened swabs used for cleaning.

Black paint on white ground contains bone black in a medium consisting predominantly of zinc stearate, aluminum soap (aluminum stearate?) and oil. There is no evidence that DEAE soaps are present in the paint. When treated with DEAE in the lab, the metal soaps are converted to DEAE soaps.

The yellowish ground contains calcium carbonate and a small amount of barium sulfate in oil.

Spectra of some samples contain weak peaks at 1615-1625 and 1315-1321, which may be from calcium oxalate or other oxalates. Oxalic acid and its salts are metabolic by products of molds, fungus, and algae.

No DEAE or DEAE reaction products were found in samples from this painting.

**"After Picasso Woman Looking in Mirror" by Harry Engel (IUAM Acc. No. 14) (Samples 693.78 to .80)**

Blue paint on white contains zinc stearate, small amount of aluminum stearate, small amount of oil, and barium sulfate.

Black material associated with the blue paint contains bone black in zinc stearate plus oil. There is much more oil in the black than in the blue paint.

White paint under the blue contains lead white in oil.

Green paint contains Pigment Yellow 36 (lead potassium zinc chromate) and calcium carbonate in a medium of zinc stearate and oil, very similar to the medium of the black paint. Since this is a green paint, there is presumably a blue pigment present also, but it was not detected.

Black material on the surface and running down into a crack contains protein, zinc stearate, trace ester, bone black, and calcium carbonate. There are cellulosic fibers attached to this material. This protein and the black pigment are associated with a crack, and could be related to a treatment of the crack, or residue of some other kind of treatment that has been retained in the crack. Also, since the protein is associated with cellulose fibers this may suggest the support is a glue sized canvas.

Blue paint and white ground from the tacking margin is identical to blue paint from the middle of the painting.

Spectra of some samples contain weak peaks at 1620 and 1316, which may be from calcium oxalate or other oxalates. Oxalic acid and its salts are metabolic by products of molds, fungus, and algae.

No DEAE or DEAE reaction products were found in samples from this painting.

**"Magdalene at her Toilete" by Gentilesci (IUAM Acc. No. 66.113) (Samples 693.81 to .85)**

Varnish contains natural resin and oil. The oil content varies from sample to sample and may be from underlying paint. No pure resin varnish was detected, all had some oil. Spectra of some varnish samples had poorly defined, weak peaks that might be from metal soaps, but not from DEAE soaps (perhaps metal driers). Treatment of the varnishes with DEAE in the lab always produced DEAE resinate.

Brown paint under the varnish contains calcium carbonate and silicates, small amount of metal soap (maybe lead soap, but not DEAE soap) in resin plus oil or oil with high acid content. The color of the sample and the presence of silicates suggests that the brown pigment is an iron earth pigment.

Brick red paint under brown paint contains calcium carbonate, silica, traces of metal soap, and resin plus oil or oil with high acid content. This medium is the same as that in the brown paint. Color and presence of silica suggest red is from iron earth pigment.

Clear material under brick red has calcium carbonate in oil and is associated with cellulose fibers suggesting that this is a calcium carbonate-oil ground applied to the canvas.

Blue paint attached to a varnish scraping contained ultramarine blue and lead white in oil.

Accretion on pulpy mass contains natural resin and oil on paper. The "medium" is the same as the varnish.

Spectra of some samples contain weak peaks at 1615-1625 and 1315-1321, which may be from calcium oxalate or other oxalates. Oxalic acid and its salts are metabolic by products of molds, fungus, and algae.

No DEAE or DEAE reaction products were found in samples from this painting.

**Etty (IUAM Acc. No. 57.34) (Samples 693.86 to .88)**

Varnish contains natural resin.

Chocolate brown paint contains calcium carbonate and lead white in oil plus resin, or oil with high acid content.

Grey-brown layer under chocolate brown contains calcium carbonate, gypsum, oil and protein.

No DEAE or DEAE reaction products were found in samples from this painting.

**"Ste. Catherine" by Zagnelli (IUAM Acc. No. 77.43) (Samples 693.89 to .90)**

Varnish contains resin plus oil.

Chocolate brown layer, immediately below the varnish contains calcium carbonate, gypsum and resin, perhaps with some oil.

Black and grey particles contain gypsum, calcium carbonate, resin, and probably some oil.

Spectra of some samples contain weak peaks at 1615-1625 and 1315-1321, which may be from calcium oxalate or other oxalates. Oxalic acid and its salts are metabolic by products of molds, fungus, and algae.

No DEAE or DEAE reaction products were found in samples from this painting.

**"Landscape" by Valtat (IUAM Acc. No. 73.14.3) (Samples 693.91 to .92)**

Varnish is poly(vinyl acetate).

Cream colored and orange paints contain lead white, trace calcium carbonate, and oil.

Fibers are cellulose like cotton or linen, not like wood (paper).

No DEAE or DEAE reaction products were found in samples from this painting.

**de Pazzi (IUAM Acc. No. 71.101) (Samples 693.93 to .95)**

The samples indicate that many materials have been used on, or much has been done to, this painting, either by the artist or during treatments.

The white spheres on the painting surface are cellulose nitrate and an ester. The ester does not appear to be drying oil and may be an ester type plasticizer for the cellulose nitrate.

Varnish has a smooth clear zone above a rough granular zone. The smooth clear zone is predominantly drying oil, with a very small amount of cellulose nitrate. The granular zone is cellulose nitrate with oil. It appears that cellulose nitrate was sprayed on, which is indicated by the spherical bodies such as are sometimes produced when varnishes are sprayed. This sprayed cellulose nitrate layer was then covered by an oil layer which encapsulated cellulose nitrate spheres, creating the granular appearance, and higher cellulose nitrate content in the lower portion of the varnish.

The layer of swirling green and yellow paint is a complex mixture containing an ester (unidentified, perhaps drying oil), zinc stearate and small amount of aluminum carboxylate like aluminum stearate, and organic pigments.

Organic pigments have very complex spectra. Many but not all absorptions in this sample match those for Color Index Pigment Yellow 3 (e.g., Hansa Yellow l0G). This is common in modern paints. For example, Grumbacher Catalog lists “Grumbacher Permanent Bright Green” as containing Pigment Green 7 (a chlorinated copper phthalocyanine), Pigment Yellow 3, Pigment Black 6 (amorphous carbon), and Pigment White 4 (zinc oxide).

Yellowish material in the red paint have spectra with spiky peaks typical of organic pigments, which were not identified.

Prussian blue was identified in several components. This, mixed with yellow pigment, may comprise a green paint.

Red paint contains oil, zinc soap, small amount of aluminum soap, and cellulose ether.

White ground on paper contains calcium carbonate, calcium sulfate, and oil. No cellulose nitrate is present in the white layer.

The cardboard is composed of cellulose. This may contain oxalates.

No DEAE or DEAE reaction products were found in samples from this painting.

**“Arctic Scene”, by Bradford (IUAM Acc. No. 68.218) (Samples 693.96 to .97)**

The varnish on top is an acrylic varnish.

Brown layer on the ground contains a sulfate like basic lead sulfate, lead white, metal soap (perhaps zinc and calcium soaps), and oil.

White ground contains lead white, oil, some lead soaps (reaction product of basic lead white and oil acids), and small amount of protein. There appear to be two layers of ground separated by a very thin red layer. There is more protein and soap in the layer below the red.

The red layer was too thin to isolate and analyze.

No DEAE or DEAE reaction products were found in samples from this painting.

**Andrea del Sarto (IUAM Acc. No. 79.101) (Samples 693.98 to .99, and .107)**

Varnish is a natural resin.

Sample 693.107 from behind the frame rabbet has poly(vinyl acetate) on the resin varnish. Poly(vinyl acetate) was not detected in any other sample from this painting.

A thin red glaze or paint is under the varnish. This appears to have oxalates.

Pale brown layer appears to be two layers, one having silica, carbonate, protein, perhaps a small amount of resin, and perhaps oxalates, the other with sulfate (perhaps calcium sulfate), carbonate, and protein.

White ground contains silica and sulfate (perhaps calcium sulfate), protein, and oxalates.

Spectra of some samples contain weak peaks at 1615-1625 and 1315-1321, which may be from calcium oxalate or other oxalates. Oxalic acid and its salts are metabolic by products of molds, fungus, and algae.

No DEAE or DEAE reaction products were found in samples from this painting.

**Thos Hart Benton Murals (Samples 693.100 to .102)**

Clear hazy top coating is acrylic resin with a small amount of protein.

Translucent brown layer under acrylic contains protein. This contains oxalates.

White ground contains calcium carbonate with no organic.

Pink paint contains calcium carbonate (may be from substrate), barium sulfate, and protein. This has hazy coating of acrylic.

Chocolate brown paint contains calcium carbonate, china clay (kaolin), and protein. The brown color of the paint and presence of clay suggest it is pigmented with iron earth colors.

No DEAE or DEAE reaction products were found in samples from this painting.

**IUAM Acc. No. 78.67.1 (Sample 693.103)**

Clear colorless particles contain lead white, metal carboxylate soap, and a small amount of oil.

No DEAE or DEAE reaction products were found in samples from this painting.

**IUAM Acc. No. 78.62.2 (Samples 693.104 to .106)**

Varnish is ketone resin like Ketone Resin N or Laropal K80.

Brown under varnish and orange under brown contains calcium carbonate, barium sulfate, china clay, and traces of ketone resin. There is very little organic binding medium in these layers.

Tan colored bottom layer contains calcium carbonate, barium sulfate, and protein.

Blue is composed of azurite, a blue copper hydroxy carbonate, with a trace of lead white, and perhaps a metal soap.

No DEAE or DEAE reaction products were found in samples from this painting.

**"#11" by Jackson Pollock (IUAM Ace. No. 75.87) (Sample 693.108)**

Crystals of efflorescence are predominantly palmitic acid with some stearic acid, and perhaps an alcohol like glycerol.

No DEAE or DEAE reaction products were found in samples from this painting.

Palmitic and stearic acids react with DEAE to form DEAE carboxylate soap (i.e., DEAE palmitate and DEAE stearate, respectively). Since there is no indication of DEAE soaps in the IR spectra, the efflorescence is not a DEAE reaction product, nor is it likely to have been caused by DEAE contamination. If it was then we would expect to see DEAE soaps, not free acids.

**"BRW1", from Lilly Library ((Samples 693.109 to .111)**

Varnish is natural resin. Some samples showed small amount of oil.

Sample 693.111 has an orange layer below the varnish which contains calcium carbonate, lead white, bone black and oil. Incompletely calcined bone black may appear orange or brown when viewed in transmitted light.

Green paint contains calcium carbonate, barium carbonate, calcium sulfate (gypsum), zinc soap, Prussian blue, and oil.

The ground appears to be three layers, a greenish white above and thin red layer, and white below. Greenish white ground contains lead white, calcium carbonate, zinc soap, and oil. The red layer was too thin to analyze. The white ground below the red has calcium carbonate, lead white, and oil, but not zinc soap.

No DEAE or DEAE reaction products were found in samples from this painting.

**“A1072”, from Lilly Library (Samples 693.112 to .116)**

Varnish is natural resin, perhaps with a small amount of oil. Small salt-like deposits on the varnish surface have the same composition.

Chocolate brown paint contains calcium carbonate, silicates from iron earths, zinc soap, oil, and perhaps oxalates.

An unidentified granular beige layer having spectra reminiscent of cellulose ethers is on the brown layer in one sample. This is covered by resin varnish.

A clear layer on brown containing protein, calcium carbonate, oil, and perhaps oxalates in on the brown in another sample. This is covered by resin varnish.

White ground below brown contains lead white, lead soap, and oil.

Spectra of some samples contain weak peaks at 1615-1625 and 1315-1321, which may be from calcium oxalate or other oxalates. Oxalic acid and its salts are metabolic by products of molds, fungus, and algae.

No DEAE or DEAE reaction products were found in samples from this painting.

**“LRM1”, from Lilly Library (Samples 693.117 to .119)**

Varnish contains natural resin and oil

Black paint contains bone black, Prussian blue, calcium carbonate, perhaps gypsum,, and oil.

Ground contains lead white, calcium carbonate, and oil.

Spectra of some samples contain weak peaks at 1615-1625 and 1315-1321, which may be from calcium oxalate or other oxalates. Oxalic acid and its salts are metabolic by products of molds, fungus, and algae.

No DEAE or DEAE reaction products were found in samples from this painting.

**“WCB” from Lilly Library (Samples 693.120 to .122)**

Varnish contains natural resin and oil.

Clear layer under varnish contains natural resin and starch.

Yellowish glaze (tiny particles (specks) in clear orange matrix) under varnish contains natural resin and starch.

Red glaze contains calcium carbonate, lead white, and resin plus oil. An unknown compound with IR peaks at 1090 and 1034 is also present.

Black paint contains bone black, calcium carbonate, and oil or oil plus resin.

Ground contains lead white, calcium carbonate and oil.

Spectra of some samples contain weak peaks at 1615-1625 and 1315-1321, which may be from calcium oxalate or other oxalates. Oxalic acid and its salts are metabolic by products of molds, fungus, and algae.

No DEAE or DEAE reaction products were found in samples from this painting.

**“R2664” from Lilly Library (Samples 693.123 to .125)**

Samples 693.123 and 693.125 have sea green paint with a single green layer containing a large amount of carboxylate soaps with peak at 1569, a small amount of oil, and calcium carbonate.

The soap in this sample has a peak at 1569 which is characteristic of DEAE soap. However, it does not have several other peaks which are also in DEAE soaps. The spectrum does not match that of reaction products of DEAE with carboxylic acids, or DEAE with oil paints. In particular, the minor ester that is present is very much less with respect to the 1569 peak, than is obtained when DEAE is reacted with a oil paint in the lab. Thus the 1569 compound is not DEAE soap, and seems to be a deliberate addition to the medium, and constitutes the major component of the medium. This looks like a mixture of the 1569 compound plus a little bit of oil, but does not look like an oil that has been partially (or completely) reacted with DEAE.

Sample 693.124 has green paint which consists of many thin blue, green and yellow layers.

A blue component contains ultramarine blue, oil, and aluminum soap. Barium sulfate is also present in some blue samples, but absent in others.

A sea green component contains barium sulfate, calcium carbonate, aluminum soap, and oil.
A number of sharp peaks in the spectrum remain unassigned and may be from green organic pigment.

Spectra of some samples contain weak peaks at 1620 and 1316, which may be from calcium oxalate or other oxalates. Oxalic acid and its salts are metabolic by products of molds, fungus, and algae.

No DEAE or DEAE reaction products were found in samples from this painting.

**Summary of results of FTIR analysis of products of reaction of DEAE with model compounds**

DEAE reacted only with the acidic components of model compounds. DEAE produced DEAE resinates from dammar by reacting with the resin acids in dammar, DEAE soaps by reacting with carboxylic acids (myristic, palmitic and stearic acid) and the acid components (fatty acids) in linseed stand oil and trilinolenic.

Ammonia and morpholine reacted with carboxylic acids in a similar way to produce ammonium and morpholine carboxylate soaps.

DEAE did not react with esters including tripalmitin and tristearin and methyl stearate.

DEAE did not react metal soaps including aluminum, calcium, sodium or zinc stearate.

The amount of reaction of DEAE with model compounds decreased with the concentration of the DEAE.

At 10000 ppm, dammar, copal, and all acids liquefied and the IR showed DEAE soaps. The methyl and glycerol esters, and metal soaps did not react (nor did they react when exposed to 100% DEAE vapors in a hanging drop apparatus).

At 400 ppm, DEAE soaps were formed from myristic acid, and to a lesser extent from palmitic acid. The myristic acid liquefied, whereas the palmitic acid was only “moistened”. Stearic acid looked unchanged and did not show DEAE soap in its spectrum. This suggests that the reaction may depend on crystallinity, being least favored for the most crystalline stearic acid.

Dammar did not react with DEAE at 400 ppm.

The DEAE appears to react with resin and carboxylic acids in a straightforward acid-base neutralization reaction to produce a DEAE salt (DEAE resinate or DEAE carboxylate soap).

DEAE does not hydrolyse or saponify triglyceride ester. DEAE will not damage oil paint media by this reaction.

DEAE does not enter into ion exchange reactions with metal soaps to replace the metal ion by DEAE ion.

The simple reaction can be written as follows:

$R^1{}_2R^2N$ + HOOR ?   $[R^1{}_2R^2NH]+$ [OOR].

where RCOOH represents carboxylic and resin acids, and $R^1{}_2R^2N$ is DEAE where $R^1$ is ethyl group ($-CH_2CH_3$) and $R^2$ is ethoxyl group ($-CH_2CH_2OH$).

## 6. Conclusion

Studies on the model compounds showed that DEAE can react with the acidic components of paintings, in particular with the resin acids in natural resin varnishes, and free fatty carboxylic acid in drying oils. However, DEAE does not react with carboxylic esters of glycerol, and therefore is unlikely to react with the triglyceride esters that comprise the major component of drying oils.

DEAE reaction products, specifically DEAE carboxylate soap, was tentatively identified in only one painting, “Peinture” by Soulages. It was found in the ground layer, but in no other layers, including an acidic oil layer on the surface, where the potential for reaction is greatest.

Small amounts of oxalate compounds, perhaps calcium oxalate, were detected in several paintings. One source of oxalic acid and its salts is metabolic by products from molds, fungus, and algae.

The analyses reported here indicate that the IUAM paintings have not been damaged by reaction with DEAE.