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THE ROOM TEMPERATURE EVAPORATION BEHAVIOR OF PURPORTED AZEOTROPES
USED AS CLEANING SOLUTIONS IN ART CONSERVATION

For the degree of   Master of Science

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THE ROOM TEMPERATURE EVAPORATION BEHAVIOR OF PURPORTED

AZEOTROPES USED AS CLEANING SOLUTIONS IN ART CONSERVATION

A Thesis

Submitted to the Faculty

of

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Carrison, Megan S. M.S., Purdue University, August 2014. The Room Temperature Evaporation Behavior of Purported Azeotropes Used as Cleaning Solutions in Art Conservation. Major Professor: John V. Goodpaster.

Finely-tuned solvent mixtures are used by art conservators for the difficult task of safely and selectively removing yellowed varnish, disfiguring grime, and discolored overpaint from the surface of oil paintings. This process is often referred to as "picture cleaning" and depends on the different solubilities of the obfuscating surface materials and the underlying paint medium. However, differential evaporation rates for the solvents used in these carefully formulated cleaning mixtures can change the potency of the mixture over time, which could potentially lead to solutions having solubility characteristics that are ineffective at cleaning, or worse yet, are deleterious to artists' oil paints. Azeotropic blends of solvents have been proposed as an alternative for maintaining consistent solvent composition throughout the evaporation process while benefiting from their high vapor pressure relative to the pure solvents. Azeotropes are specific combinations of two or more solvents at a precise concentration that behave as a single solvent, maintaining a constant composition in both the liquid and vapor phases. The use of purportedly azeotropic solvent blends has appeared in the art conservation literature for the cleaning of historic objects and paintings. However, these solvent

mixtures are taken from tables of azeotropic compositions given at their boiling point. We have studied one of these solutions, a 19:81 vol% mixture of isopropanol and n-hexane. For the first time, the actual evaporation behavior of this purported azeotropic mixture was followed in detail at room temperature conditions. Through the use of rudimentary vapor pressure measurements, gravimetric analysis, as well as sophisticated compositional determinations of both the liquid phase and headspace of evaporating mixtures by gas chromatography, this particular cleaning solution has been shown to be zeotropic (i.e. NOT an azeotrope) under the conditions typical of conservation studios. The true room temperature azeotropic composition was found instead to contain half as much isopropanol at 9.5 vol%. Art conservators should therefore be dubious of purportedly azeotropic mixtures reported at boiling points well above room temperature. Individual azeotropic cleaning blends are best determined chemically prior to their use in art restoration. Furthermore, the introduction of a model paint film to the evaporating room temperature azeotrope was shown to further confound its behavior, calling into question whether solvent systems can be configured to evaporate with constant composition from the surface of an artwork.

CHAPTER 1. INTRODUCTION

Paintings, like all artwork, suffer from the ravages of time and require periodic

maintenance to preserve their aesthetic qualities. Varnishes yellow and crack, dirt

accumulates, retouchings discolor, and grime builds up. These affronts to the intent of

the artist require occasional cleaning of the picture to remove the offending materials (1).

This daunting task falls to art conservators, professionals who utilize their knowledge of

art history, artists' materials, and chemistry to concoct tailored treatment approaches for

each individual artwork. Art conservation is a unique field that much like forensic

science is not fully appreciated by the general public who rarely witness it in action. The

profession incorporates scientific analysis into the study of art to ensure that the

conservation of historic objects is done as effectively and safely as possible in the effort

to preserve the integrity of our cultural patrimony.

Oil paintings are one of the most common types of artwork that conservators must

clean in order to preserve the original appearance intended by the artist. An oil painting

is normally a multilayered structure; a support is regularly covered with a white ground

material, often toned with an imprimatura layer, onto which a sketch is drawn and later

painted in multiple thick or thin layers of pigmented medium composed of a vegetable oil

such as linseed, walnut, poppy, or more recently, safflower and soya oils (2). The

triglycerides in these unsaturated oils polymerize to form a tough network film through a

complex series of oxidative crosslinking reactions (3-5). Oil paints have historically

been modified with other adjuvants including waxes and natural resins to adjust their

rheological and aesthetic qualities. The topmost surface of oil paintings can be further

"finished" through the application of thin, transparent glazes of oil paint, and at least

since the 1700s, with a natural resin terpenoid varnish based on tree exudates, e.g. mastic,

dammar, or colophony.

   With age, these paintings can appear to have a yellowed look as their varnishes

oxidize, crosslink, and deteriorate. Other factors can contribute to layers of grime on the

surface of an oil painting, such as exposure to cigarette smoke or the collection of dust

from improper display or storage conditions. The conservator's interventions used to

remedy these situations are loosely referred to as "picture cleaning," although technically

removal of dirt and the stripping of old varnish are two separate tasks (1). The job of

cleaning oil paintings is a difficult one because of the innumerable possible combinations

of artists' materials, varnish resins, and accumulated grime. Navigating the differences in

solubility for these various materials, conservators often create tailored solvent solutions

to safely remove the dirt and aged varnish while being innocuous to the medium

underneath. This thesis explores scientifically the physical behavior of one approach to

solvent cleaning of oil paintings; the use of purportedly azeotropic cleaning solutions

chosen to maintain their chemical composition throughout the evaporative process.

1.1 Solvent Cleaning

   Conservators rely on an arsenal of cleaning approaches for the paintings under their

care (1, 6, 7). Attention is always given to the use of the least toxic, least invasive

methods that will achieve the desired effect. These techniques include many so-called "dry" cleaning materials to remove or reduce dirt and grime, for example the use of vinyl erasers (8), cosmetic sponges (8), dry ice blasting (9), and even bread crumbs (9). A wide array of aqueous solutions are also utilized ranging from simple saliva cleaning on a cotton swab to complicated aqueous gels loaded with chelators, ionic strength agents, and pH modifiers (10). However, organic solvents have long played an indispensable role in the cleaning of oil paintings to remove varnish coatings (4, 11, 12). These solvents are rolled across the surface of the painting on a cotton swab wound around a wooden skewer and provide a brief interaction between coating and solvent. Although "solubility" is often discussed in the field of conservation, this brief interaction usually leads only to swelling of the varnish or dirt layer rather than true dissolution (13). The conservator relies on the mechanical action of the cotton bud to remove the swollen or gelled varnish and dirt while the residual solvent evaporates from the painting's surface.

Historically, some highly toxic and potentially damaging solvents like dimethylformamide, morpholine, and benzene were used to remove or reform aged varnishes and to clean painted surfaces (14, 15). These and other organic solvents present certain known risks to oil-based paints. The oil paint medium may be leached of some of its unbound components like free fatty acids, which serve a plasticizing role in the paint film and can lead to embrittlement of the coating in even the short interaction time with the liquid (3, 4, 12, 15-17). Additionally, organic solvents that penetrate and swell paint lower the mechanical properties of the cured film (11, 12, 18-20). Cleaning this softened surface with a cotton swab saturated with solvent can be harmful, causing the softened paint to be disturbed, exposing underlying pigment particles, and

occasionally removing thinly applied paint glazes (21). However, significant effort has been expended in the field of conservation science to understand the impact of solvents on oil paints and to devise safer means of utilizing solvents in varnish removal from paintings.

A common approach to cleaning oil paintings with organic solvents is to fine-tune the solubility characteristics of a solvent mixture to address the overlying varnish and grime while being far enough from the solubility characteristics of oil paint so as not to affect it (7, 15). These formulation strategies combined with judicious control of evaporation rate and solvent dwell time have further refined the science of picture cleaning. Solvent mixtures were also proposed as a less toxic alternative for the cleaning of oil paintings, achieving similar level of cleaning efficiency as a harmful solvent by blending two less dangerous ones (22, 23).

The use of these finely tuned solvent mixtures presents a potential problem though because the vapor pressures, and therefore evaporation rates, of the two components may be radically different. Typically, the solvents used in mixtures consist of a weaker solvent, known as the "restrainer" solvent (14, 15) and a stronger solvent that is more effective at swelling and dissolving old varnish, overpaint, and grime (22). The restrainer solvent is one that is often unable to clean the surface of oil paintings successfully when used on its own, but acts to mitigate the strong solubility characteristics of the more powerful solvent. The latter solvent is not generally used alone, or at least not without great care, since its power to disrupt the varnish and dirt could also extend to the oil paint medium underneath (15). This relationship between paint medium, aged varnish and dirt, and solvent choice can be better understood when examining their solubility parameters.

1.1.1   Solubility Parameters

Solubility parameters attempt to quantify, characterize, and predict the miscibility of

solvents and the solubility of solutes based on experimental measurements of the

cohesive energy density (CED) of pure liquids. The CED represents the combined

intermolecular interactions of the liquid phase that must be overcome in order to create a

solution. The history of solubility theory as it applies to artists materials has been

summarized in detail by several authors in the conservation literature (11, 23-27). A brief

overview here will suffice to lay out the theory by which paintings conservators approach

cleaning and varnish removal on oil paintings.

The Hildebrand solubility parameter (∂) was proposed by Joel H. Hildebrand as a

numerical value of the solvent strength, defined as the square root of the cohesive energy

density (Equation 1.1) to describe the solvency behavior for a particular solvent (28).

$$\partial = \sqrt{c} = \left[\frac{\Delta H - RT}{V_m}\right]^{1/2} \text{ (Equation 1.1)}$$

where the solubility parameter is ∂, c is the cohesive energy density, ΔH is the heat of

vaporization, R is the gas constant, T is the temperature in Kelvin, and V_m is the molar

volume. The units of measurement for the solubility parameter ∂ are hildebrands and

they were originally derived from units of cohesive energy density, calories/cm^3, as

determined experimentally by boiling pure liquids and measuring the heat required to

volatilize a specific volume of liquid. This generated a spectrum of solvent "strengths"

based on their CED values (Table 1.1) spanning weak to energetic cohesiveness. The

nature of "strong" or "weak" solvent requires a point of reference of course, which for

paintings conservators generally relates to the action of the liquid on the swelling of oil

paints. The theory predicts that solvents of similar CED will be miscible since each

solvent has the ability to form similar levels of intermolecular bonds with the other

solvent as exist between the molecules of the same solvent. Those liquids distant on the

spectrum will not be able to generate favorable energetic mixing to create solutions. The

same holds true for polymeric materials and solutes, and hence Hildebrand parameters

become predictive of solubility of these materials provided enough information is known

about the components of the potential solution. Ten common solvents used for cleaning

purposes in conservation are listed in Table 1.1 in increasing order of their Hildebrand

parameter.

	Hildebrand Solubility Parameters (Burke)	
Solvent	$\partial/cal^{1/2}cm^{-3/2}$	∂ (SI)/MPa$^{1/2}$
n-Hexane	7.24	14.9
Toluene	8.91	18.3
Acetone	9.77	19.7
Methylene chloride	9.93	20.2
Isopropanol	11.60	23.8
Cellosolve ® (2-ethoxyethanol)	11.88	21.9
N,N-Dimethylformamide	12.14	24.7
Ethanol	12.92	26.2
Methanol	14.28	29.7
Water	23.50	48.0

Table 1.1: Hildebrand solubility parameters for 10 common solvents used in conservation.

Values listed in (∂) are derived from cohesive energy densities (calories/cm^3) while

values listed in international units (∂ SI) are derived from cohesive pressures. As a point

of reference regarding solvent "strength," the average Hildebrand solubility parameter for aged linseed oil is approximately 9.4 cal$^{1/2}$ cm$^{-3/2}$, meaning that solvents with a Hildebrand parameter near that value will be "strong," e.g. methylene chloride, while those at some distance, like n-hexane, will appear "weak" in their swelling action.

Although Hildebrand parameters capture the magnitude of the CED for solvents, they do not describe how that energy is partitioned into particular classes of molecular interactions. Following the adage "like dissolves like," it is not enough that two materials share a similar Hildebrand parameter, but rather that they share the same magnitude of cohesive energy and have similar partitioning of intermolecular forces for interactions to exist between two solvents (24). This refinement of solubility theory was developed by Charles M. Hansen, and the three Hansen solubility parameters attempt to partition the CED of Hildebrand (∂_t^2) into components of dispersion force (∂_d^2), hydrogen bonding (∂_h^2), and polarity (∂_p^2), as shown in Equation 1.2 (29-31).

$$\partial_t^2 = \partial_d^2 + \partial_p^2 + \partial_h^2 \text{ (Equation 1.2)}$$

With the separation of the Hildebrand parameter into three components (Table 1.2), the interactions that occur between non-ionic molecules are much more accurately estimated and explained (24). These solubility parameters are useful in understanding the miscibility behavior of solvents, as well as their effects on a variety of materials found in artwork. The Hansen parameters for the ten previously mentioned common conservation solvents are listed in Table 1.2, which includes the total Hildebrand parameter (∂_t^2), the

dispersion component (∂_d^2), the polar component (∂_p^2), and the hydrogen bonding

component (∂_h^2). Although Hansen's system enhanced the solubility prediction for resins

and polymers, its three dimensional nature lacked the ability to be easily communicated

in the early 1960s when solubility theory was making its way into the conservation field

(24).

Solvent	Hansen Parameters for Solvents at 25ºC (Hansen)			
	Total Hildebrand Parameter (∂_t^2)	Dispersion Component (∂_d^2)	Polar Component (∂_p^2)	Hydrogen Bonding Component (∂_h^2)
n-Hexane	14.9	14.9	0.0	0.0
Toluene	18.2	18.0	1.4	2.0
Acetone	20.0	15.5	10.4	7.0
Isopropanol	23.5	15.8	6.1	16.4
Methylene chloride	20.3	18.2	6.3	6.1
Cellosolve® (2-ethoxy ethanol)	-	16.2	9.2	14.3
N,N-Dimethylformamide	24.8	17.4	13.7	11.3
Ethanol	26.5	15.8	8.8	19.4
Methanol	29.6	15.1	12.3	22.3
Water	47.8	15.6	16.0	42.3

Table 1.2: Hansen parameters for 10 common solvents used in conservation at 25ºC.

Fractional parameters, determined from the three Hansen components, were used by

James P. Teas in 1968 to simplify Hansen's solubility system (32). However, by using

fractional (percentage) parameters of the three components of CED, the Teas system

ignores the overall magnitude of the intermolecular interactions. The emphasis is shifted

instead to the relative manner in which these interactions are distributed among

dispersion forces (f_d), polarity (f_p), and hydrogen bonding (f_h). As a result, these three

fractional parameters are additive and their sum will always be 100% (Equation 1.1.3).

$$f_d + f_p + f_h = 100 \text{ (Equation 1.1.3)}$$

Table 1.3 lists the Teas fractional solubility parameters for the same ten conservation

solvents listed previously.

Solvent	Fractional Solubility Parameters (Horie)		
	$100f_d$	$100f_p$	$100f_h$
n-Hexane	100	0	0
Toluene	80	7	13
Acetone	47	32	21
Isopropanol	41	16	43
Methylene chloride	59	21	20
Cellosolve®(2-ethoxyethanol)	41	23	36
N,N Dimethylformamide	41	32	27
Ethanol	36	18	46
Methanol	30	22	48
Water	18	28	54

Table 1.3: Fractional solubility parameters for 10 common solvents used in conservation.

Teas fractional solubility parameters can be used to construct a two-dimensional

ternary graph on which to plot solubility data. This two-dimensional projection of the

three-dimensional solubility parameter provided conservators with a graphic scheme that

was easy to commit to memory and was functional for predicting, plotting,

communicating, and calculating solubility parameters for all types of liquids, resins,

polymers, and paints. Teas charts are constructed as triangular ternary graphs, with three axes rotated at 60°and spanning 0-1.0 of the associated intermolecular interaction (Figure 1.1). The highest value of 1.0 for one scale will correspond to the lowest value of 0 for the others. For the most part, solvent interactions are dominated by dispersion forces and so most solvents are therefore concentrated in the lower right corner of the Teas charts at the high end of the dispersion axis. Despite the many criticisms of Hansen's and Teas' solubility theories (25, 33, 34), this triangular chart persists in conservation and provides a common point for discussion of cleaning and varnish removal for all conservators.
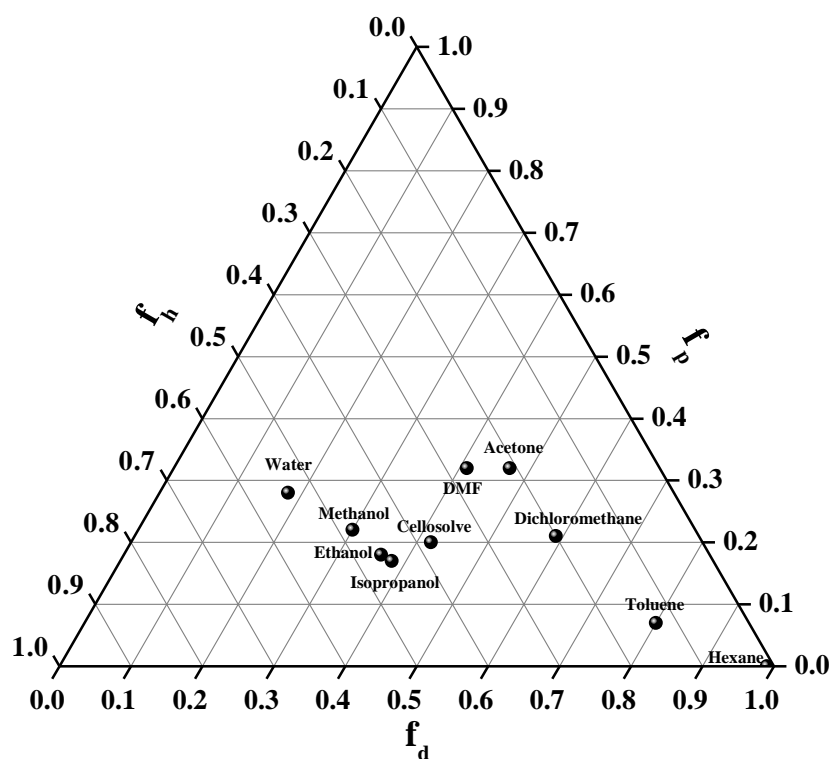
Figure 1.1: Teas chart indicating the fractional solubility parameters of 10 common conservation solvents.

Teas charts can be used to plot not only pure solvents but also art materials including polymers, resins, varnishes, and paints. Because of the range of conformations and homologs of these oligomeric and polymeric species, their coordinates on the Teas chart are not single points, but rather a solubility "window" covering a region of the graph. Since these materials cannot be volatilized in order to determine a CED experimentally, their solubility windows are determined empirically by observing the effect that different solvents have on the material in question (26). Observing the dissolution or swelling of the solute in a specific solvent will determine whether that solvent falls within the solubility window of the polymer or paint. Plotting all of the good solvents for a polymer will delineate its solubility window and suggest other solvents or solvent mixtures that will similarly dissolve the solute or swell the paint medium. The Teas chart below (see Figure 1.2) plots the solubility windows [approximated from (35)] for aged, polymerized linseed oil pigmented with white lead ($2PbCO_3.Pb(OH)_2$) (red, 60% swelling) and the natural resin varnish shellac (green). In addition, the fractional solubility parameters for the ten solvents mentioned previously are also shown for comparison. It must be noted that solubility windows for natural products like vegetable oils and insect resins are dynamic and shift with aging, oxidation, and other degradation. Generally, this trend enlarges the solubility window slightly to the lower left, showing the increasing contribution of polarity and hydrogen bonding.
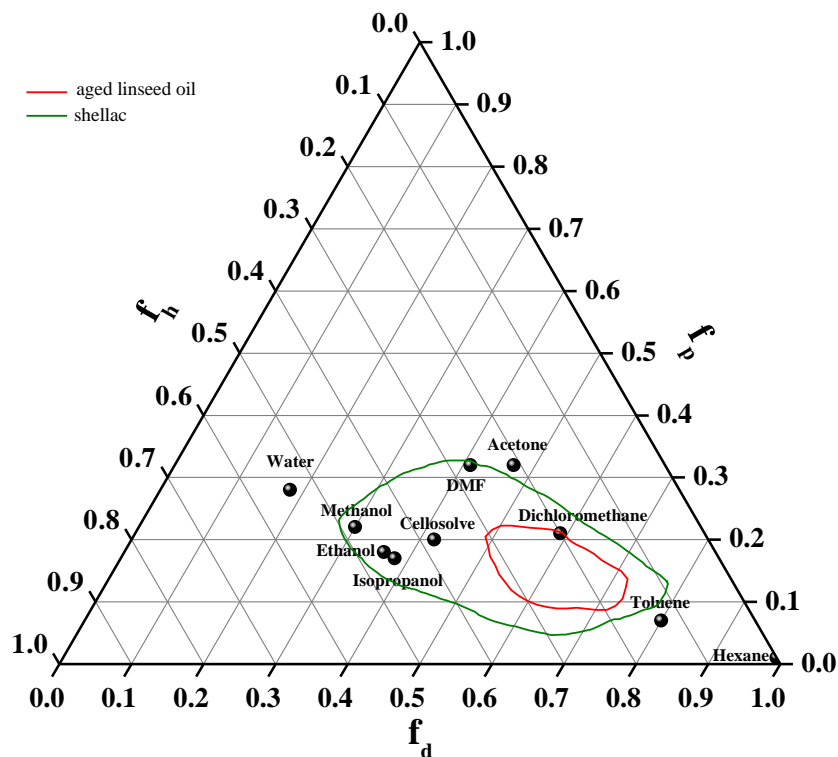
Figure 1.2: Teas chart showing the solubility windows for a well polymerized linseed oil film aged 14 years (red, 60% swelling) and shellac (green) along with fractional solubility parameters of the 10 common conservation solvents mentioned previously.

From a practical viewpoint, conservators use Teas charts to choose solvents that will dissolve or soften a varnish for removal while skirting around the solubility window of the underlying paint. With a limited number of solvents on hand and an eye to safety for the artwork and the conservator, this often requires a carefully concocted solvent blend. Blended solvents can also be fine-tuned for other important effects like evaporation rate, which might allow for safely working within the solubility window of the underlying medium due to rapid evaporation limiting the solvents' effects to the artwork's surface coating (4, 14, 15). In the chart above, the use of solvents to the left of the oil paint

swelling region in red are generally avoided because a highly oxidized oil paint film could be sensitive to these polar cleaners. To remove a shellac varnish, the conservator might choose a solvent that lies within or near the shellac solubility window, but to the right of the oil paint swelling region. Toluene could be used in this instance to slowly soften the shellac varnish for removal by swab rolling (22).

Another important use of the chart is to determine solvent blends that can replace expensive, toxic, slowly evaporating, or unpleasant solvents without sacrificing dissolving power. Teas parameters are linearly additive for binary or tertiary mixtures and can therefore be easily determined graphically by drawing a line connecting the two desired solvents and finding the point on the line that corresponds to the volume fractions of the mixtures (24, 26). Calculations based on the fractional parameters of the pure solvents in the mixture and their corresponding volume percentages can also be performed to generate the fractional parameters for a specific mixture of the solvents (11, 24, 26). For instance, a 19 vol% solution of isopropanol (f_D=38; f_P =17; f_H=45) in n-hexane (f_D=100; f_P =0; f_H=0) would have solubility parameters of f_D=82; f_P =5; and f_H=13.   It is interesting that this mixture falls close to the solubility parameters of the aromatic solvent toluene (see Figure 1.1), thus allowing ready substitution for that solvent. Recently computer software, like *The Modular Cleaning Program, Solvent Solver, Trisoly, and Triansol* has automated these calculations (36-38). The chart below, Figure 1.3, shows the Teas coordinates for isopropanol and n-hexane, as well as the 19:81 vol% mixture, which lies predictably one fifth of the way between n-hexane and isopropanol on the dotted blue line. These solvents are shown superimposed over the linseed oil and shellac solubility windows from above. A solvent mixture such as the 19

vol% isopropanol in n-hexane could be used in lieu of toluene with the added benefit of a

faster evaporation rate, and therefore more control over the interaction of the cleaning

solvent with the shellac varnish (Augerson 2000).

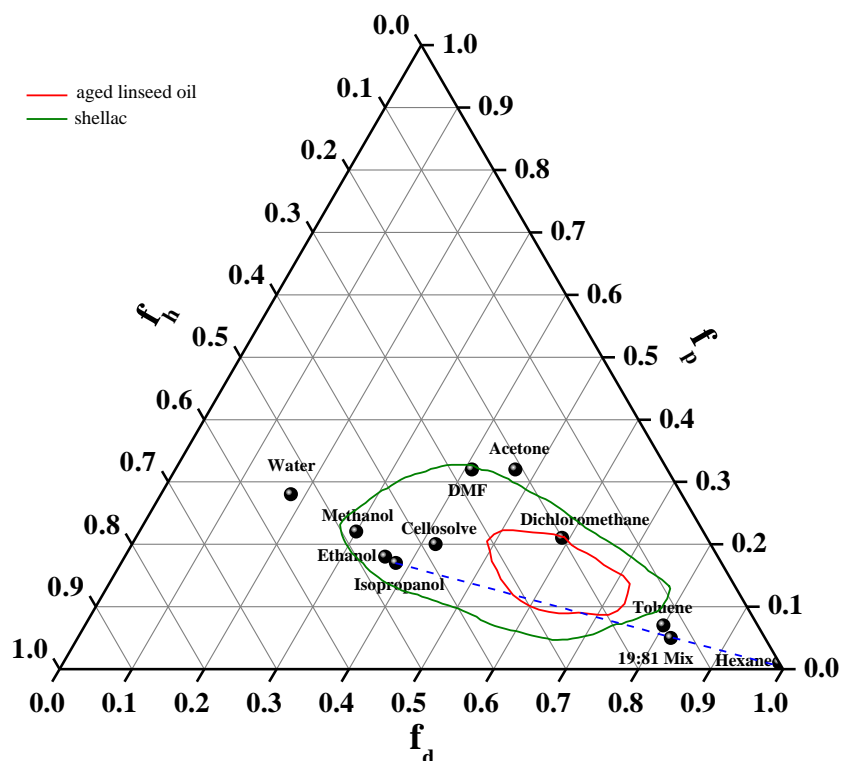Figure 1.3: Teas chart showing the solubility windows for polymerized linseed oil and
shellac along with fractional solubility parameters of 10 common solvents as well as a
19:81 vol% mixture of isopropanol in n-hexane.

1.2 Conservation Concerns with Cleaning

The care and cleaning of oil paintings is approached with great caution by

conservators. Their professional code of ethics requires that careful planning, testing,

and documentation proceed, accompany, and complete each interventive treatment of an artwork (39).   Historically, this was not always the case. Many harsh cleaning solutions have been proposed for the removal of varnish from paintings, and these approaches have invariably left many artworks scarred and in need of substantial restoration (1, 15, 21, 40).

Only in recent decades have the consequences from cleaning materials such as these been realized. Even the use of more appropriate cleaning solutions can have negative effects on an artwork, and result in the "skinning" of the top layer of paint from the surface (13, 21). All these factors contribute to the difficulty of the task at hand for a paintings conservator. Assessing the condition of the artwork is first and foremost, followed by identifying the materials used. Chemical analysis can assist in this task (41), although analytical facilities are not always available to the conservator who must otherwise rely on intuition and solubility testing in an inconspicuous area (15). A typical oil painting can include not only the paint medium but overlying varnishes and restoration paint as well as adjuvant components such as waxes and resins added to the medium by the artist for practical or aesthetic reasons. Some of these components may be undesirable and require selective removal through judicious choice of cleaning solvents or mixtures, while others should be preserved and not suffer from solvent leaching or blanching. The mixing of varnish-like materials by artists' into their oil paints broadens the medium's solubility window and can make cleaning extremely difficult or even impossible (1, 13, 21).

In any cleaning intervention there is the potential for unexpected consequences (21). Often the exact nature of the offending materials slated for removal is unknown.

Additionally, even the most carefully crafted cleaning mixture may prove dynamic, both

in its ability to flow into unwanted areas through cracks and crevices in the varnish or

paint (13), but also in its changing chemical composition. Differential evaporation rates

are an inherent risk for conservators using solvent blends. The possibility exists that the

rapid loss of one solvent could shift the solubility parameter of the solution to a point that

it becomes ineffective as a cleaning solvent, or worse yet, that it becomes dangerous to

the paint medium. This concern has led some paintings conservators to advocate for the

use of azeotropic cleaning solutions, i.e. specific solvent mixtures that evaporate at

constant composition (22, 27, 42-45).

1.3 Azeotropes as Cleaning Solutions

Azeotropes are a mixture of two or more solvents that maintain the same composition

in the vapor state as they do in the liquid state at equilibrium (46, 47). As a result, the

components will boil as if they were a single solvent, maintaining the same composition

throughout their volatilization. This makes azeotropes impossible to separate by means

of simple distillation (46, 48-50). Azeotropes form due to the molecular interactions

between dissimilar structural moieties in the participating solvents (48). These molecular

interactions can be attractive or repulsive in nature, resulting in a mixture with boiling

point that is either elevated (high-boiling or positive azeotrope) or depressed (low-boiling

or negative azeotrope), respectively, in relation to the boiling points of the pure solvents.

Repulsive forces, for instance the intermolecular interactions between the hydroxyl in

water and the alkyl group in ethanol, lead to an increased vapor pressure for the mixture

and therefore a low-boiling azeotrope is formed for these two solvents. Conversely, if the

interactions are attractive, as in the concentrated nitric acid-water system, the vapor

pressure is reduced and a positive azeotrope is formed. Azeotropes are important

industrially since they represent a major hurdle to purifying solvents through distillation

(48, 50, 51). The CRC Handbook lists hundreds of positive and negative binary

azeotropes with the compositions given at their boiling point (52), and similar tables are

available in the chemical literature (47).

The wide range of solvent azeotropes makes their use possible as cleaning solutions

for a variety of media and varnishes found in painted artwork. Augerson (2000) has

reviewed the tabulated azeotropic compositions in the CRC Handbook and identified

certain binary mixtures whose calculated solubility parameters should be appropriate for

varnish removal on oil paint (22, 42). His work on 16th century painted sleighs from the

collection of the Château of Versailles recognizes the advantages of these purportedly

constant evaporation compositions for maintaining cleaning efficiency while avoiding the

possibility of overly harsh mixtures developing through evaporation. In addition,

negative (low-boiling) azeotropes offer lower boiling points and higher vapor pressures

than the pure component solvents, giving conservators another tool to limit the

interaction of the cleaner to only the surface residues. The use of azeotropes in paintings

conservation has been described further by Stavroudis (2006) and Saunders (2008), and

the potential for azeotropic cleaning solutions has even been incorporated into software

used by paintings conservators to guide their cleaning efforts (37).

Despite the possible benefits of using azeotropes to clean paintings, the solvent

blends recommended so far may not deliver on that promise. The composition of a

solvent mixture that will behave azeotropically depends on both temperature and pressure

(53). The azeotropically boiling mixtures given in the CRC are not necessarily azeotropically evaporating mixtures, at room temperature, despite the fact that the two solvents might still form an azeotrope under evaporative conditions at some other composition.

The study of solvent systems that evaporate at constant composition is not new (49, 54-60). For example, the coatings industry has manipulated solvents for polymeric materials in order to achieve specific rheology and surface finishes in paints and lacquers (55, 56, 61). In order to avoid unexpected aesthetic and practical issues, the solvents used to deliver the coatings must maintain a constant composition and therefore controlled solubility of the coating material. A review of the literature did not produce any previous studies that covered the purported azeotropes used in art conservation however.

A potential issue with using azeotropic mixture compositions reported at their boiling points as cleaning solvents for oil paintings is that they are actually utilized at room temperature, approximately 21ºC, in a typical conservation studio. This could present a potential problem in the cleaning of oil paintings. If the purported boiling point azeotropic mixtures used do not behave azeotropically at room temperature, they may not evaporate at constant composition. The stronger solvent may become overly concentrated in the residual liquid as the mixture evaporates, which could potentially damage the surface of the oil painting as it adsorbs into the paint itself. Similarly, if the changing composition leaves the cleaning mixture ineffective, then the treatment of the painting is inefficient or incomplete.

To explore the room temperature evaporation behavior of purported azeotropes used in paintings conservation, a single system was chosen as an initial scientific investigation. The 19:81 vol% mixture of isopropanol and n-hexane is listed in the CRC Handbook (1979) as being a negative azeotrope with a boiling point of 61ºC. The boiling points of isopropanol and n-hexane are 82.3 ºC and 68.7 ºC respectively. This azeotropic mixture has been used for cleaning purposes by conservators and is referenced many times in the conservation literature (22, 42-45). For example, it has been used successfully to clean varnishes from multiple painted French sleighs at the Château of Versailles (22, 42). Given the popularity of this azeotrope, as well as the large difference in its reported boiling point versus room temperature, it serves as a good mixture for an initial study.

CHAPTER 2. MATERIALS AND METHODS

2.1 Solvents

Although conservators often use commodity or laboratory-grade solvents in the
cleaning of oil paintings, all experiments reported here were performed using the highest
purity solvents available. Isopropanol (Optima) was acquired from Fisher Scientific with
a listed purity of ≥99.98% (Fisher Scientific, Waltham, MA). Two types of n-hexane
were purchased from Sigma Aldrich (Sigma Aldrich, St. Louis, MO). The one used for
the initial vapor pressure studies was Chromasolv® HPLC-grade solvent of ≥95% purity.
During the course of the experiments a higher purity version at ≥97% was made available
and used exclusively thereafter. It is important to note that many conservators refuse to
use hexane due to its neurotoxicity, often choosing to use the much less harmful heptane
instead. However, when conservators do use hexane, it is often the laboratory grade
"hexanes", which is an unpurified blend of all its isomers. It is unknown at this point
what effect this subtle difference may have on azeotrope formation. The literature values
for the boiling point, density, molecular weight, and vapor pressure for the solvents can
be viewed in Table 2.1

	Molar Weight (g/mol)	Density (g/mL at 25ºC)	Boiling Point (ºC)	Vapor Pressure (mmHg at 20ºC)
Isopropanol	60.10	0.785	82	33
Hexane	86.18	0.659	69	132

Table 2.1: Physical properties of isopropanol and n-hexane (52).

2.2 Vapor Pressure

Room temperature vapor pressure measurements for 29 samples spanning 0-100% isopropanol, with a greater number of these samples falling in the range near the purported azeotrope, was completed using a rudimentary Raoult's Law kit. The ambient conditions were 21ºC and approximately 743 mmHg. A 25 mL polyethylene bottle with a rubber stopper containing two bored holes in the top was used as the test vessel. A 3 mL plastic pipette holding the test solution and a short length of PVC tubing were inserted into the adjacent holes. The PVC tube was connected to a Vernier Gas Pressure Sensor attached to a Vernier LabPro Data Collection Interface (Vernier Software and Technology, Beaverton, OR). This interface was connected through a USB port to an Asus Net Book for collection and storage of data. The software used to collect the vapor pressure data was LoggerPro 3. The vapor pressure kit is shown in use in Figure 2.1.

The plastic bottle was held in a glass dish during data collection in order to prevent the heating of the solvents in the bottle through contact with body heat. Care was taken in order to ensure consistency when applying force to the rubber stopper in the top of the plastic bottle so as not to influence the pressure measurements; solutions with a high vapor pressure tended to exert enough pressure to expel the rubber stopper. Vapor pressure measurements were conducted by taking up 3mL of the desired solvent into the

pipette bulb and inverting the pipette in the rubber stopper to keep the liquid in the bulb.

As the rubber stopper was inserted into the plastic bottle, force was applied to push the

stopper down into the bottle. The pipette bulb was then squeezed to release the liquid as

the plastic bottle was turned upright and set in the glass dish. Gentle shaking of the test

chamber helped to establish a stable vapor pressure quickly.

Figure 2.1: Raoult's Law vapor pressure kit.

Each sample was analyzed separately using the vapor pressure kit with measurements

taken every second for approximately 30 seconds until the vapor pressure values began to

plateau, and each trial was performed in triplicate. Prior to each measurement, the

components of the kit that came into contact with solvents were dried with nitrogen. The

maximum vapor pressure reached during analysis was recorded for each of the 29 trials

and was used to plot the vapor pressure (mmHg) versus isopropanol concentration (volume percent) with error bars representing ± 1 standard deviation from the 3 replicate measurements.

2.3 Evaporation Weight Loss

The masses of 12 solvent compositions, spanning 0-100% isopropanol in 10% increments and including the purported azeotrope, were collected over time in weight loss studies to determine evaporation rates. In this initial study, a single measurement was performed for each sample composition. A Mettler Toledo XP56 analytical balance (± 0.01 g) with BalanceLink automated software (Mettler Toldeo, Columbus, OH) was used to measure and log the gravimetric data. The analytical balance was positioned under an adjustable exhaust trunk 10 inches away to remove solvent vapor without creating a large draft over the samples. Small petri dishes (60 x 15 mm) were used to hold 5 mL initial aliquots of each solvent mixture as it evaporated on the analytical balance. The weight loss experimental set up can be seen in Figure 2.2. Each sample was allowed to evaporate as the pool of liquid lost mass linearly over time, keeping a constant droplet radius, i.e. "pinning," until the pool of liquid began to shrink and the evaporation became dependent on the radius of the liquid. The evaporation of the initial 5 mL aliquots was tracked for approximately 23 minutes. A second, more detailed study included 11 solvent compositions narrowly bracketing the purported azeotropic composition, spanning 0-30 vol% isopropanol in 3% increments. The same materials and methods were used for the second study, although the trials were each repeated in triplicate.

Figure 2.2: Evaporation weight loss experimental set-up.

The evaporation rate of the solvent compositions in both studies was found by plotting the mass in grams as a function of the time and calculating the slope. The slope for each sample was plotted as a function of isopropanol concentration in volume %. In the second study, the point at which the liquid began to pull away from the sides of the container was seen to occur sooner for the 0-30% isopropanol samples, so only the first 700 seconds of data was used. The average evaporation rate of the triplicate data was plotted as a function of isopropanol concentration with error bars representing ±1 standard deviation.

2.4 Evaporation Profiles: Gas Chromatography (Liquid Samples)

The liquid chemical composition profiles of evaporating solvent mixtures were studied by gas chromatography with thermoconductivity detection (GC-TCD). A complicated evaporative cell-GC apparatus has been used in the literature to make dynamic measurements of residual solvent from evaporating solutions (55), but the studies reported here utilized simpler static measurements of residual liquids from solutions allowed to evaporate to specific weight loss intervals. Solvent compositions ranging from 2-20 vol% isopropanol in 2% increments, including the purported azeotrope, were freshly prepared in 21 mL aliquots. Volumetric pipettes of 1, 2, 4, 5, 10, and 20 mL (Wilmad-LabGlass, Vineland, NJ) were used to pipette volumes greater than and equal to 1 mL. An automated eVol™ XR Dispensing System (Thermo Fisher Scientific, Inc.) was used to pipette volumes smaller than 1 mL. Each solvent composition was stored in scintillation vials (Wheaton) wrapped with Parafilm.

Ten 2 mL aliquots of the stock solution for each solvent composition were pipetted using the eVol™ dispenser into ten separate pre-weighed 2 mL glass shell vials (Fisher Scientific). Each sample and vial was weighed again using a Mettler Toledo XP56 analytical balance then capped to prevent premature evaporation. These ten duplicate samples would allow for 10 evaporation experiments to be performed, each terminating at a different predetermined percent weight loss. From the starting weight of each sample, the expected masses of these samples after periodic weight losses ranging from 10 to 85% were calculated. By monitoring the evaporation of each sample on a balance, the pre-determined weight loss intervals would indicate when each sample evaporation should be stopped by tightly capping the appropriate vial.

All 10 shell vials for a specific solution composition were placed into the fume hood together and their caps removed to allow for the contents to evaporate to the pre-determined weight loss %. The hood sash was completely closed, to achieve rapid, even evaporation of the solutions. Figure 2.3 shows the shell vials for one set of samples before evaporation, and another set of samples after evaporation. Each evaporation profile for the 23 solvent compositions, consisting of the 10 shell vials per composition, occurred in approximately 75-120 minutes.
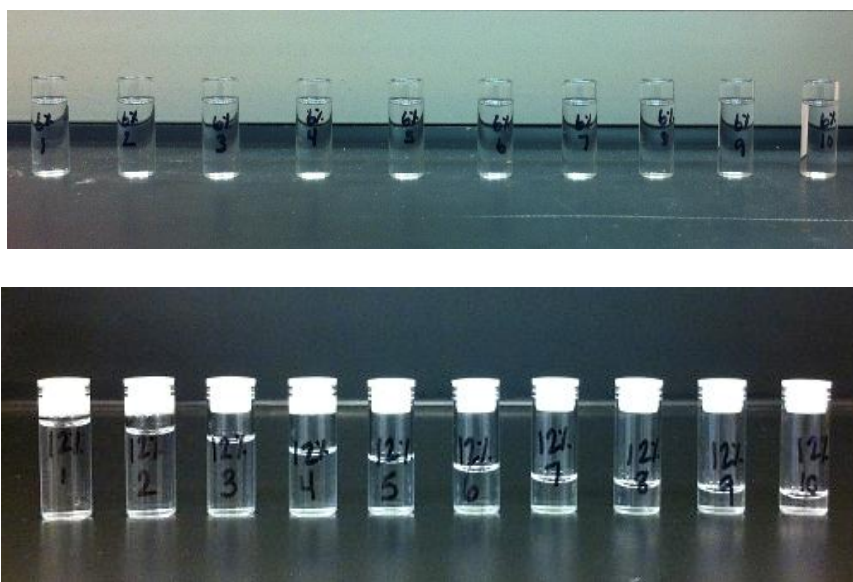

Figure 2.3: Evaporation sample images. The top image shows ten identical 2 mL aliquots of 6 vol% isopropanol solution in n-hexane during evaporation. The bottom image shows the vials for 12 vol% isopropanol solution in n-hexane after evaporation to the pre-determined 10-85% weight loss intervals.

When all samples had reached their set weight loss percentages, the evaporation series
for that sample composition was complete and sampling for GC-TCD liquid analysis
could be done. Using the eVol™ dispensing system, 100 µL of each of the remaining
solvent samples was pipetted into autosampler vials in triplicate for each of the 10 weight
loss intervals for all solvent compositions. For the samples that had reached 80 and 85%
weight loss during evaporation, too little sample was available for a full 100 µL aliquot,
and so only 50-70 µL could be pipetted into each triplicate vial. The autosampler vials
used were the 2 mL glass, 9 mm short-cap screw-thread type with PTFE/silicone septa
(Restek Corporation, Bellefonte, CA) and a 300 µL polyspring, glass vial insert (Fisher
Scientific).

A Thermo Fisher Trace GC with a TriPlus AS autosampler (Thermo Fisher, Waltham,
MA) was used to analyze the liquid samples. An Agilent Technologies DB-ALC1
column (30 m x 0.32 mm ID x 1.8 µm film) was used to effect baseline separation of the
isopropanol and n-hexane solvents (Agilent Technologies, Santa Clara, CA). Optima-
grade methanol (Fisher Scientific) was used as the wash solvent. The syringe was
washed with methanol prior to a sample rinse and injection, and again after each sample
injection. The injected sample was 0.5 µL, followed by 1 µL of air. The carrier gas was
helium, at a flow of 1 mL/min. The GC inlet temperature was 200ºC. The oven program
started at 60ºC, with a temperature ramp of 20ºC/min, to a final temperature of 100ºC
with an 8 min hold. Total run time for each analysis was 11 min. The inlet was operated
in the split mode, with a He split flow of 60 mL/min. The TCD block temperature was
110ºC, with a transfer temperature of 100ºC. The TCD was operated in constant voltage
mode with a filament voltage of 5 V. The He makeup gas flow was 19 mL/min and the

He reference flow was 20 mL/min. The TCD bridge was balanced automatically to get

an output reading of 1,000 and an offset value of 0. Data were analyzed using Thermo

Xcalibur Qual Browser version 1.0.1.3 (Thermo Fisher). Chromatogram peaks were

integrated automatically using the ICIS mode with manual adjustments made to the

baseline.

2.5 Evaporation Profiles: Gas Chromatography (Headspace Samples)

The evaporation profiles of 5 solvent compositions, including 2, 9, 9.5, 10, and

20vol% isopropanol in n-hexane, were obtained by headspace analysis GC-TCD. A

complicated evaporative cell-GC apparatus has been used in the literature to make

dynamic measurements of solvent loss from evaporating solutions (54), but the studies

reported here utilized simpler static measurements of equilibrated headspace from

solutions allowed to evaporate to specific weight loss intervals. Each solvent

composition was prepared in 550 mL aliquots as described previously and stored in 1 L

glass bottles with tightly fitted caps wrapped with Parafilm. The 5 solvent compositions

used in this study were chosen based on the results of the previous study using liquid

injection GC-TCD (vide infra).

Ten 50 mL aliquots of the stock solution for each solvent composition were pipetted

using a 50 mL volumetric pipette into ten separate pre-weighed 60 mL amber glass

bottles with tightly fitting lids (Fisher). Each sample and bottle was weighed again using

a Mettler Toledo XS4002S Delta Range toploading balance, then capped to prevent

premature evaporation. From the starting weight of each sample, a percent weight loss

value was calculated, ranging from 10-85% weight loss as before. This would determine

when each sample would be capped and the evaporation halted. The 50 mL aliquots were poured into separate pre-weighed 50 mL glass beakers and placed in the fume hood as before to evaporate. Each beaker was weighed periodically until it had reached its pre-determined weight loss percentage. At that point, the sample was poured back into its original 60 mL glass storage bottle and tightly sealed until analyzed. Each evaporation for the 5 solvent compositions occurred in approximately 75-120 min.

When all samples for a specific solvent composition had reached their set weight loss percentages, the evaporation profile for that composition was complete and samples for headspace GC-TCD analysis were prepared. Triplicate 2 mL samples were prepared from the remaining solvent in each weight loss stage using a volumetric pipette. These were added to headspace autosampler vials (20 mL, 20mm, Restek) for each of the 10 evaporation samples for all solvent compositions tested. Aluminum crimp caps with PTFE/silicone septa (Restek) were tightly fitted to the vials.

The same GC-TCD, autosampler, and chromatographic conditions as before were used for the headspace analysis, with the exception that a nitrogen purged headspace injection module was used in lieu of the liquid injection module. The sample incubator was kept at ambient temperature, although the vials were agitated for 40 sec prior to analysis, and the headspace syringe was maintained at a constant 40ºC. A 1 mL injection volume was used for all samples. The chromatographic data were analyzed as previously described.

2.6 Introduction of a Paint Film to the Binary Azeotrope Mixture

The last phase of this project sought to explore the effect of a commercial paint sample on the evaporation of an experimentally determined room temperature azeotropic solution of isopropanol and n-hexane. A cobalt blue hue oil paint (#T321-7, Grumbacher Academy Oil Color) was chosen as a representative paint sample. The product contains an alkali refined linseed oil medium with ultramarine, copper phthalocyanine blue, carbazole dioxazine, bone black, and titanium white pigments. The paint was applied to silicone release Mylar using a BYK thin film applicator at 8 mil wet coating thickness. The paint was first aged at room temperature for 2 months to achieve "touch dryness" then aged at 50% relative humidity and 70ºC for 2 weeks to simulate as close as possible natural aging conditions over several decades (3, 13).

Four 20 mm circular samples of the aged paint film were removed from the Mylar backing and added to headspace autosampler vials. Into three of these vials, 500 µL of a 9.5 vol% solution of isopropanol in n-hexane was added using the eVol dispenser; the fourth paint sample was not covered with solvent. Three additional headspace vials without a paint film were also charged with 500 µL of the same solvent mixture. The solvent volume was chosen based on the calculated amount of solvent that would totally vaporize in the 20 mL headspace vial (Equation 2.1).

$$Vs = \frac{10^{\left(A - \left(\frac{B}{T+C}\right)\right)} Vc}{RT} * \frac{M}{\rho} \quad \text{(Equation 2.1)}$$

where Vs is the amount of solvent to add; A, B, and C are the Antoine Equation

parameters; Vc is the volume of the container; R is the ideal gas constant; T is the

temperature in degrees Kelvin; M is the molecular weight of the solvent; and ρ is the

density of the solvent. The calculated amount, 28.5 µL, was adjusted to 500 µL so that

there was enough solvent to completely cover the paint film in the vial. These samples

were analyzed using the same equipment and protocol as the previous headspace

samples.

CHAPTER 3. RESULTS AND DISCUSSION

3.1 Vapor Pressure

A low-boiling binary solvent azeotrope should have the highest vapor pressure of any

mixture of the two solvents. As an initial exploration of the room temperature azeotropic

composition for isopropanol and n-hexane, rudimentary vapor pressure measurements

were made of a range of mixtures spanning 0 to 100 vol% at ambient laboratory

conditions. The vapor pressure of 29 solvent compositions ranging from pure hexane to

pure isopropanol, with greater numbers of samples clustered around the purported

azeotrope composition, are shown in Figure 3.1. In general, there is a decrease in vapor

pressure as the concentration of isopropanol increases, an expected result considering the

lower volatility of isopropanol relative to n-hexane. The experimental vapor pressure for

pure n-hexane and isopropanol were determined to be 157.9 mmHg and 51.7 mmHg,

respectively (at 21ºC). The literature values for pure hexane and isopropanol at 20ºC are

132 mmHg and 44 mmHg, respectively (52). Although the highest average vapor

pressure recorded was for the solution having 17 vol% isopropanol, the general trend

when one considers the entire data set suggests a maximum vapor pressure exists at

approximately 10 vol% isopropanol. Because of the rudimentary nature of the vapor

pressure apparatus, a more comprehensive gravimetric analysis focused on this region of

the composition range to elucidate further the room temperature behavior of the solvent
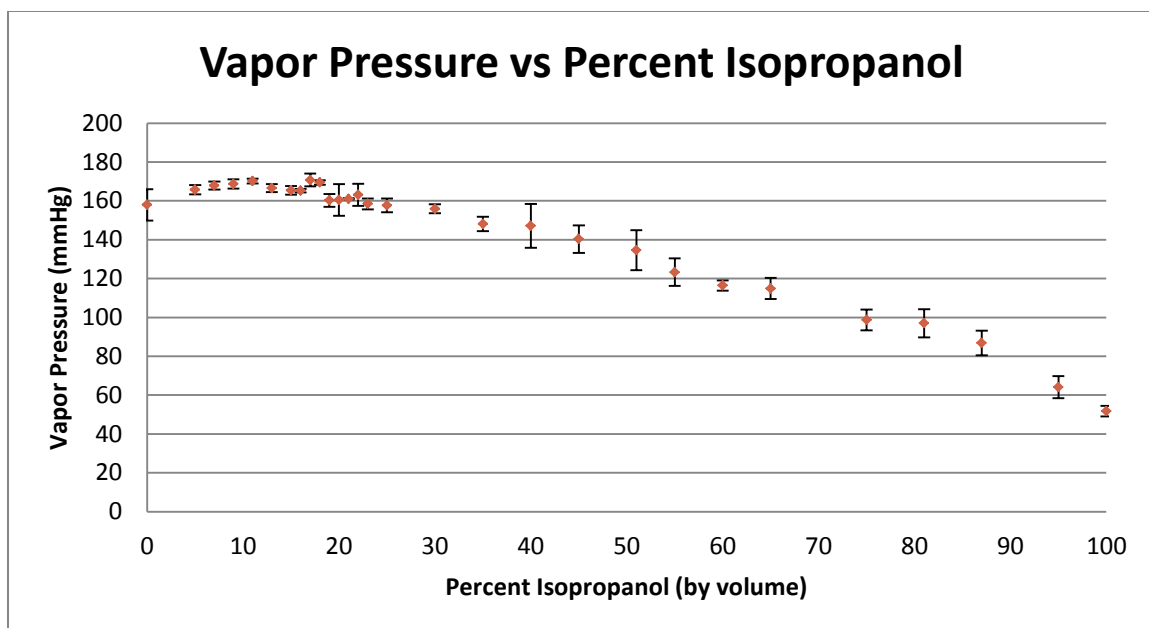
mixtures.

Vapor Pressure vs Percent Isopropanol

Figure 3.1: This graph shows vapor pressure versus percent isopropanol for solvent compositions ranging from 0-100 vol% isopropanol.

3.2 Evaporation Weight Loss

A solvent mixture with the highest vapor pressure at room temperature, i.e. the constant composition evaporating solution or room temperature azeotrope, should also experience the fastest evaporation rate under controlled conditions of air flow. Two evaporation weight loss trials were done for a range of isopropanol and n-hexane mixtures. The first trial consisted of single samples ranging from pure n-hexane to pure isopropanol in 10% increments, including the purported azeotrope at 19 vol% isopropanol. The weight loss in grams versus evaporation time in seconds was plotted for each of these 11 samples. The slopes of the best fit lines through each of the data sets was taken as that composition's initial evaporation rate, and these values are plotted in Figure 3.2 against increasing isopropanol concentration (Figure 3.2). An abrupt

minimum, meaning the most negative slope, occurs noticeably at 10 vol% isopropanol,

confirming the vapor pressure trend discussed above.
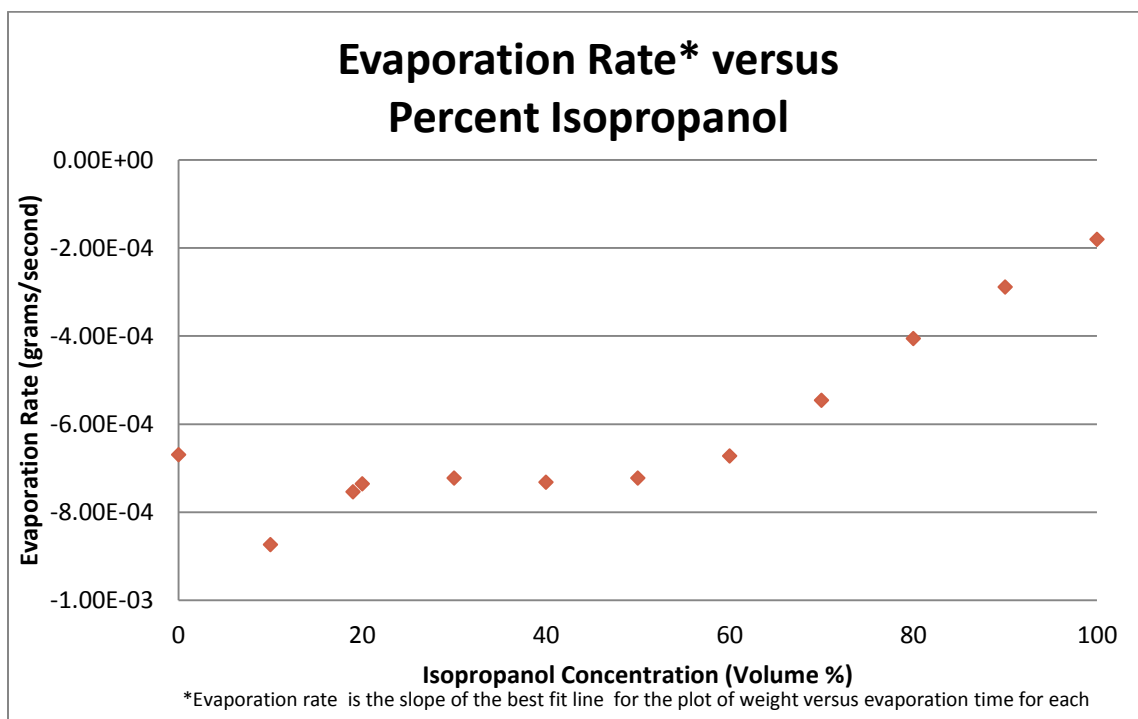
Figure 3.2: This graph shows the single measurement of evaporation rate versus percent isopropanol for the first evaporation weight loss trial.

A second evaporation weight loss trial was performed on triplicate samples in a

narrower concentration range spanning 0-30 vol% isopropanol. The average slopes from

the best fit lines of each triplicate set of gravimetric data were plotted against the vol%

isopropanol in Figure 3.3. The vertical error bars represent ±1 standard deviation. The

sample with 9 vol% isopropanol exhibits the most negative slope, or fastest evaporation

rate, suggesting this is closest to the room temperature azeotropic composition. This

behavior agrees with the earlier vapor pressure data showing a general trend having the

maximum vapor pressure around 10 vol% isopropanol. Somewhat erratic behavior is noticed in the area of the fastest evaporating solution based on the measured deviation in the data. The increase in the standard deviation could indicate the sensitivity of the evaporation rate to the concentration of isopropanol in the area immediately surrounding the mixture having the highest vapor pressure.
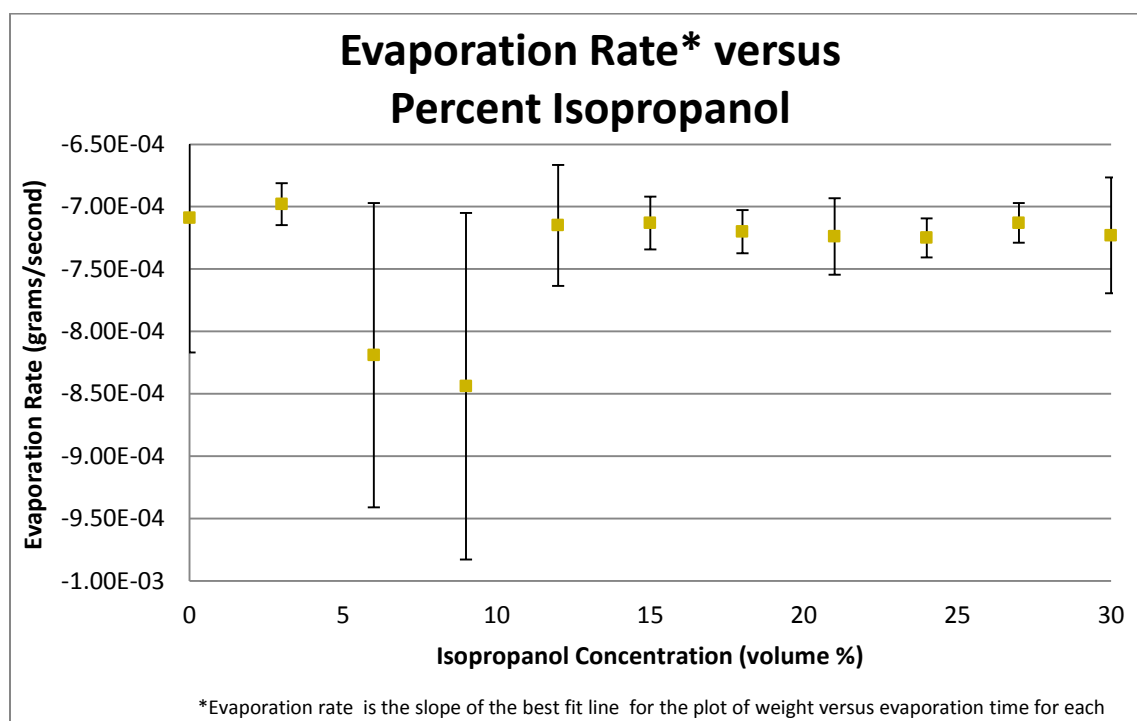
Figure 3.3: This graph shows the evaporation rate versus percent isopropanol for the second evaporation weight loss trial, with a minimum seen at 9% isopropanol.

F-tests were conducted to compare the variance between the 6 vol% and 9 vol% isopropanol samples and the rest of the data, respectively. Two-sample F-tests for variance were done between 3 vol% and 6 vol% isopropanol, with the result being that they did not have significant variation with 95% confidence. The same tests were

performed between the 9 vol% and 12 vol% isopropanol samples, with the result being

that they also did not have significant variation. From these tests, it can be concluded

that the results for the 6 vol % and 9 vol % isopropanol samples can be included with

confidence, and any variation in the data seen in the error bars can be attributed to the

samples themselves. T-tests performed on the same data pairs also showed that the

values were not statistically anomalous and that all the results should be considered.

Summarizing the gravimetric analysis, it is important to note that the purported azeotrope

at 19 vol% isopropanol does not exhibit the fastest evaporation behavior – and thus the

highest vapor pressure – in ether of the two evaporation weight loss trials.

3.3 Evaporation Profiles: Gas Chromatography (Liquid Samples)

Vapor pressure and evaporation weight loss experiments showed that samples much

lower in isopropanol composition than the purported azeotrope exhibited higher vapor

pressures and faster evaporation rates. These data suggest that the room temperature

azeotrope should fall somewhere near 10 vol% isopropanol rather than at the purported

value of 19 vol%. This suggestion was next followed chemically by analyzing the liquid

and the vapor phases of an evaporating solution to show which isopropanol-hexane

mixture evaporated at constant composition. Samples ranging from 2-20 vol%

isopropanol were evaporated to set weight loss intervals, with the residual liquids being

analyzed by GC-TCD. Changes in the composition of the mixtures during evaporation

highlight the zeotropic or azeotropic behavior of the different compositions.

Chromatograms were analyzed for each of the original 11 samples ranging from 2-20

vol% isopropanol. Figure 3.4 shows a representative chromatogram for the sample

concentration of 9.5 vol% isopropanol. The peaks at 3.49 and 4.14 min belong to isopropanol and n-hexane, respectively. The peak occurring at 2.88 min corresponds to residual methanol from the needle rinse. All sample chromatograms were identical, except for changes in peak area for the two solvents of interest.
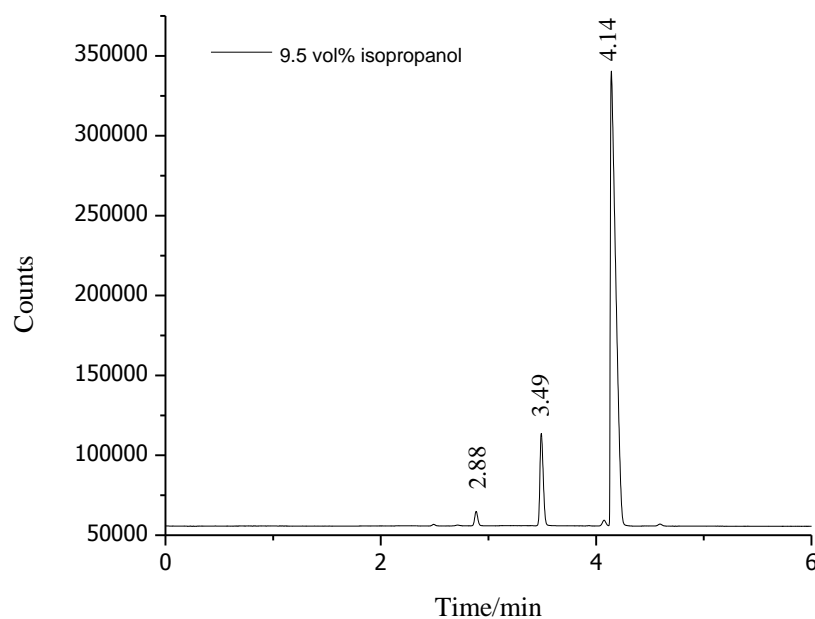
Figure 3.4: Representative chromatogram of the 9.5 vol% isopropanol solution in n-hexane with peak retention times.

Each triplicate set of data from the residual liquid phase was integrated to generate peak areas for the n-hexane and the isopropanol peaks. The ratio of the isopropanol peak area to the n-hexane peak area was tabulated for each triplicate sample, and then the average and standard deviation were calculated for each evaporating composition at each weight loss interval. The average ratio of the isopropanol to n-hexane peak area was

plotted against the percent weight loss for the 11 samples and is shown in Figure 3.5.

The error bars represent ±1 standard deviation for the triplicate measurements.
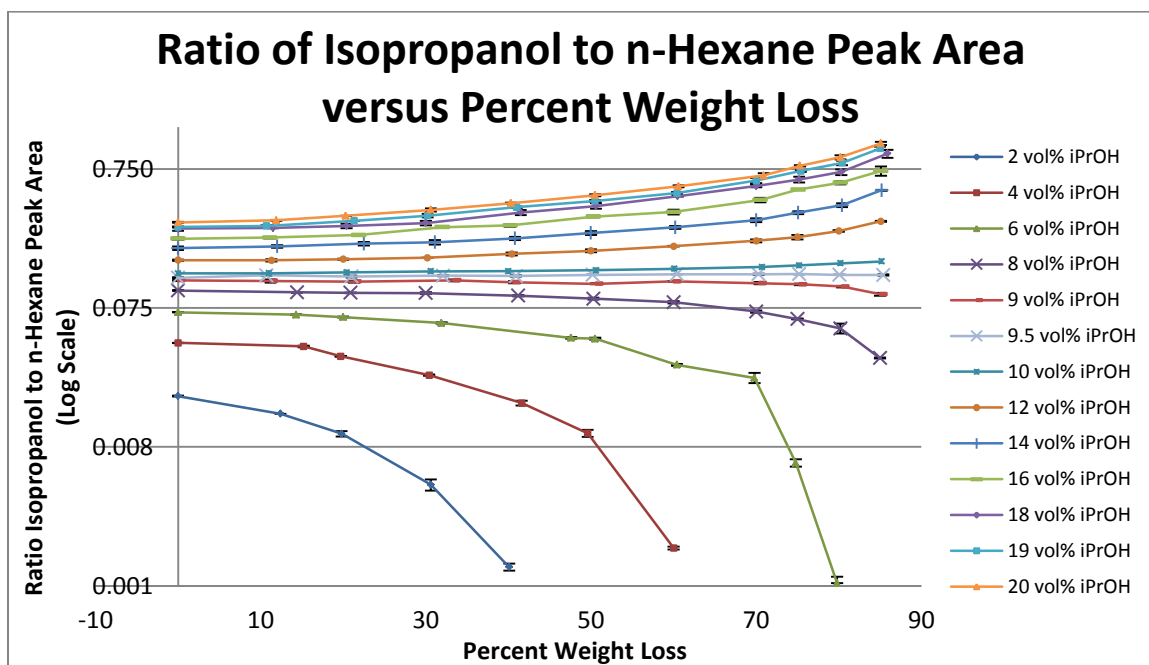
Figure 3.5: This graph shows the ratio of isopropanol to n-hexane peak area versus the percent weight loss for all 13 compositions studied.

If a sample evaporates at constant composition, as would be expected for a room temperature azeotrope, then one can assume the ratio of the residual liquids' isopropanol to n-hexane peak as measured by GC-TCD would remain constant throughout the evaporation profile. A large negative deviation can be seen in the ratio for the 2, 4, and 6, and 8 vol% isopropanol samples, which shows that these mixtures became richer in n-hexane over the course of their evaporation.

The 12 through 20 vol% isopropanol samples exhibited positive deviation, including the purported azeotrope at 19 vol% isopropanol. This confirms that the purported azeotrope does not exhibit constant composition as it evaporates at room temperature. Like the other samples just mentioned, the purported azeotrope becomes enriched in isopropanol with increasing evaporation, which might explain its action in the removal of shellac from historic sleighs at Versailles (22, 42, 43). Laboratory tests showed blonde shellac to be only sparingly soluble in toluene and in a 19 vol% isopropanol in n-hexane solution. The flakes of shellac were softened enough to become cemented together in these solutions, but did not fully dissolve or swell. Allowing the 19:81 mixture of the two solvents to evaporate to half the original volume appeared to increase the mixture's ability to solubilize the shellac, perhaps due to the increasing concentration of isopropanol in the mixture as it evaporated.

In the range of 9-10 vol% isopropanol in Figure 3.5, little deviation occurs in the solvent ratio, with the least change in the ratio occurring at 9.5 vol% isopropanol. This is the experimentally determined room temperature azeotrope. Similar solubility experiments with this azeotrope and blond shellac flakes showed no action on the resin, suggesting the true room temperature azeotrope would be ineffective at removing shellac.

3.4 Evaporation Profiles: Gas Chromatography (Headspace Samples)

Analysis of solvent mixtures of varying isopropanol concentration over the course of their evaporation profile using GC-TCD on the residual liquid showed that the purported 19 vol% isopropanol solution was *zeotropic* at room temperature. In fact, a solution with almost half that amount of isopropanol, 9.5 vol%, appeared to evaporate at constant

composition as expected of an azeotrope. In order to confirm whether this composition truly behaved azeotropically, the equilibrium vapor phase of the residual solvent mixture was analyzed by headspace GC-TCD over the course of its evaporation to determine if the headspace also demonstrated constant composition.

The samples chosen for headspace analysis narrowly bracketed the 9.5 vol % isopropanol sample identified as a likely room temperature azeotrope through the aforementioned analysis of liquid samples. For each of the 5 samples, the residual liquid left from each sample after the set evaporative weight loss interval had been reached was analyzed to characterize the equilibrated headspace over the liquid using the GC-TCD. Each triplicate set of data was integrated to determine the peak areas of both solvents. The ratio of the isopropanol peak to the n-hexane peak was calculated for each triplicate sample, and the average was calculated for each stage in the weight loss. The average ratio of isopropanol to n-hexane peak areas was plotted against the percent weight loss as before, and the data is shown in Figure 3.6. The error bars represent ± standard deviation in the triplicate data. It can be seen that the error bars for the headspace data are larger than those for the liquid data, which reflects the lower reproducibility of the headspace sampling technique relative to that of liquid injections.

In this case, the 9, 9.5, and 10 vol% isopropanol samples exhibited little to no variation around a central ratio of 0.12. The headspace sampling protocol used here appears to be unable to detect the small changes in the headspace composition expected from small changes in vol% concentration of isopropanol. Samples evaporated from starting compositions with larger deviations from the expected 9.5 vol% room temperature azeotrope did show the expected positive (20 vol% isopropanol) and

negative (2 vol% isopropanol) deviations as observed in the liquid sample analysis. From this headspace data, it can be seen that the 9.5 vol% isopropanol sample, which showed no deviation in the residual liquid phase during evaporation, also showed minimal deviation in the vapor phase during evaporation.
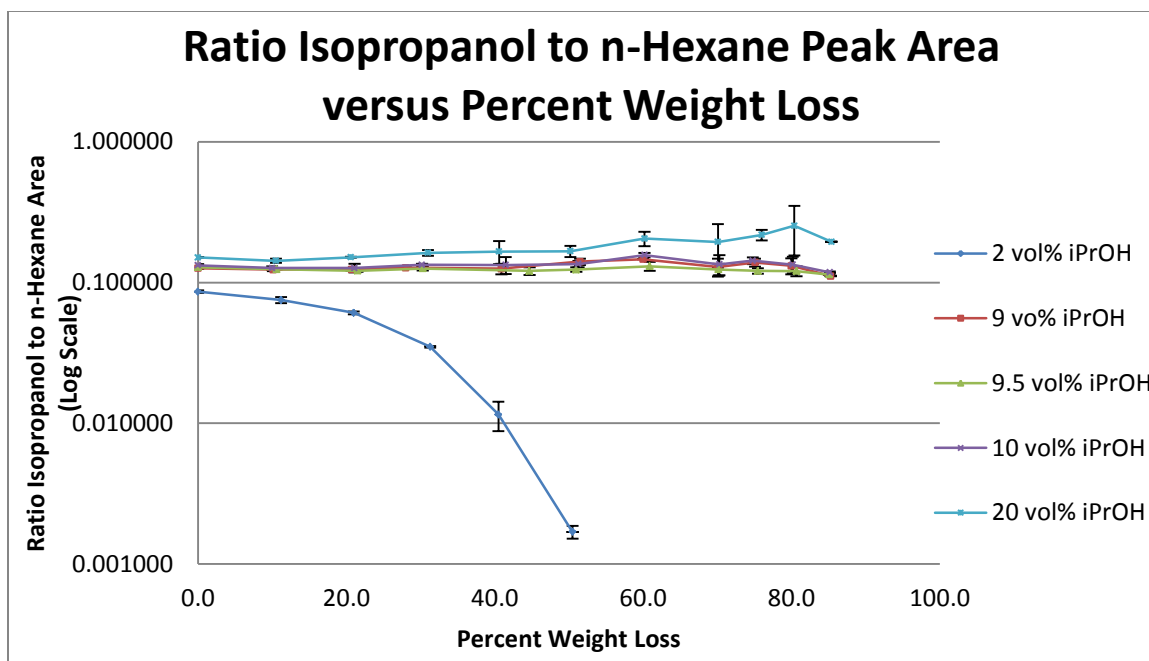
Figure 3.6: This graph shows the ratio of isopropanol to n-hexane peak area in headspace analysis versus percent weight loss for samples ranging from 2 to 20 vol% isopropanol.

3.5 Introduction of a Paint Film to the Binary Azeotrope Mixture

The previous liquid and headspace GC-TCD analysis of a range of evaporating solutions having varying isopropanol concentrations pinpointed the room temperature azeotrope of the isopropanol-hexane system to be 9.5 vol% isopropanol, well below the boiling point azeotrope at 19 vol%. When used in paintings conservation, however, this azeotrope would be introduced onto a third component of the system, an oil paint film

potentially with a natural or synthetic resin varnish. These latter materials, which would normally be only loosely characterized chemically, are expected to disturb the azeotrope as each has solubility characteristics which could lead to differential adsorption of the solvent components. In the isopropanol-hexane system, the alcohol is expected for instance to have a slightly higher affinity for oil paints and will slightly swell the paint film as it is adsorbed into the coating (4, 19, 20, 34). This loss of isopropanol is expected to break the azeotrope and lead to zeotropic behavior, adding a further complication to the use of azeotropes in paintings conservation.

An exploratory test was devised to test the potential of paint and varnishes to complicate the use of azeotropic cleaning solutions. In order to determine if this was the case, the headspace of the 9.5 vol% isopropanol in n-hexane azeotrope was compared to the headspace of that same sample in the presence of a representative paint film. A previous analysis of just the paint film found that no volatiles or semi-volatiles were outgassed by the paint that might complicate the analysis. The average ratio of isopropanol to n-hexane peak area was calculated for both sets of samples, i.e. the vials containing only the azeotrope and the vials containing the azeotrope with a paint film.

Figure 3.7 compares the peak ratios observed for the experimentally determined room temperature azeotrope when analyzed: (a) by liquid injection, (b) by headspace over a 2 mL aliquot, (c) by headspace over a 500 μL aliquot, and (d) by headspace of the same volume of solvent in the presence of a thin oil paint film. The two previous evaporation studies showed that the 9.5 vol% isopropanol in n-hexane solution evaporated at constant composition with no deviation noticed in the peak area ratio with weight losses out to 85%. This defines an azeotropic solution (48). Inspection of the

ratios themselves, 0.124 for (a) the liquid sample and 0.128 for (b) the vapor phase, over the larger aliquot of residual solvent suggests that the composition of the two phases is not identical. This can be explained though by the method of analysis and the concentration of the two samples analyzed. GC split flow inlets can experience partitioning of highly volatile samples with preference for the split being shared unevenly among sample components (62).   The larger concentration of sample in the 5 µL liquid injections can lead to a preferential loss of isopropanol, the lower volatility solvent, in the GC inlet as it volatizes to a gas, thus consistently underestimating the amount of alcohol in the liquid sample.
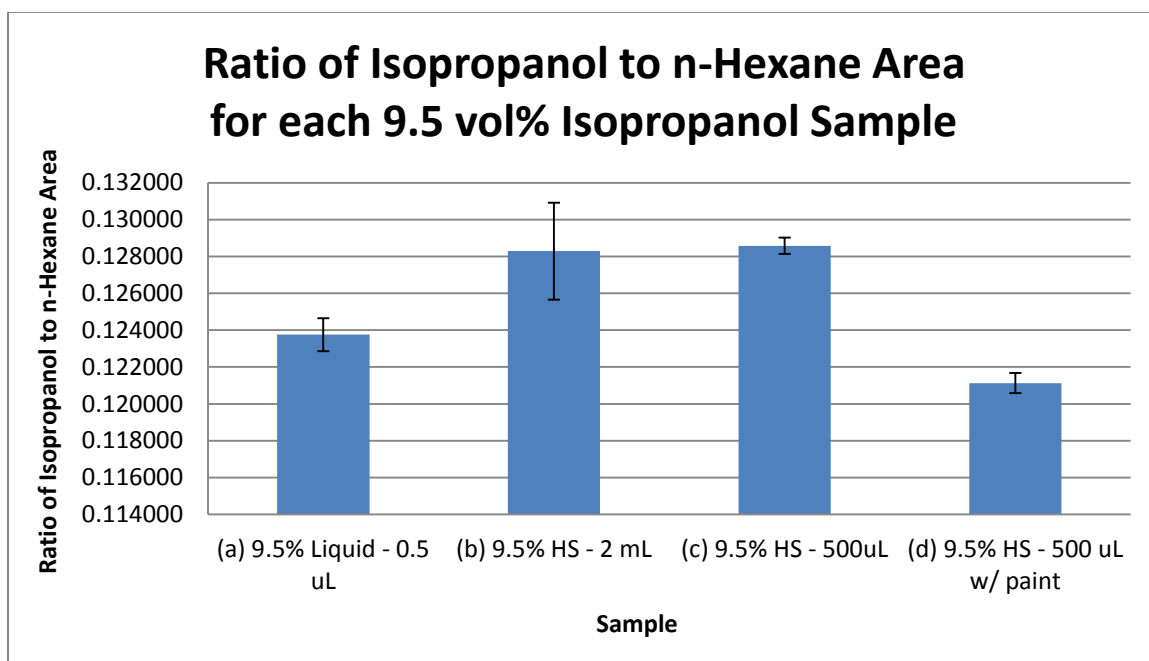
Figure 3.7:   The ratio of isopropanol to n-hexane peak area for the (a) residual liquid, (b) headspace over 2 mL residual liquid aliquot, (c) headspace over 500 µL aliquot, and (d) headspace over 500 µL aliquot in the presence of a thin paint film.

For the headspace analysis of the pure solvent mixtures, (b) and (c), the ratio is nearly identical. This indicates that regardless of the volume of liquid in the headspace vial, 2 mL or 500 μL, the ratio of the area of isopropanol to n-hexane vapor is similar. However, when the peak ratio of (c), the small volume of liquid analyzed by headspace, is compared to the same volume applied to the surface of an oil paint film, the composition of the headspace differs significantly. The lower ratio indicates that there is a smaller amount of isopropanol present in the vapor phase, consistent with its greater affinity for oil paints (4).

CHAPTER 4. CONCLUSIONS AND FUTURE WORK

A purported azeotrope used in the conservation of oil paintings has been shown to behave drastically differently under room temperature conditions than would be expected at its boiling temperature. Vapor pressure and weight loss experiments hinted that the boiling point azeotropic mixture, a 19:81 vol% mixture of isopropanol and n-hexane, was not azeotropic under room temperature evaporation conditions. Evidence of an ambient azeotrope composition closer to 10 vol% isopropanol argued for further investigation of the binary mixture in this concentration range. Further analysis of evaporating solutions with the use of GC-TCD refined the ambient azeotrope composition to be approximately 9.5 vol% isopropanol.

While the usefulness and cleaning ability of the purported azeotropic mixture of isopropanol and n-hexane is not being disputed (22, 42), it is important to clarify that it does not behave azeotropically, and therefore does not benefit from the main advantage of maintaining constant composition. The rapid positive deviation in the ratio of isopropanol to n-hexane suggests that this mixture quickly grows stronger in isopropanol, leading to greater solvency for many artists' materials including the shellac varnish for which the purported azeotrope was so useful in removing (22).

While the purported azeotrope was useful in removing shellac varnish, there are various other room temperature azeotropes in the coatings literature, determined experimentally from constant evaporation systems, which could also be useful in the

removal of shellac. The figure below, Figure 4.1, is similar to one discussed previously (Figure 1.3) showing solvent mixtures plotted alongside common solvents and artists' materials, and shows the addition of several azeotropic mixtures. The fractional solubility parameters of the azeotropes were used to calculate the Teas values in the program Solvent Solver, based on the physical property data obtained from the CRC and plotted as the mol% values given in the literature (36).
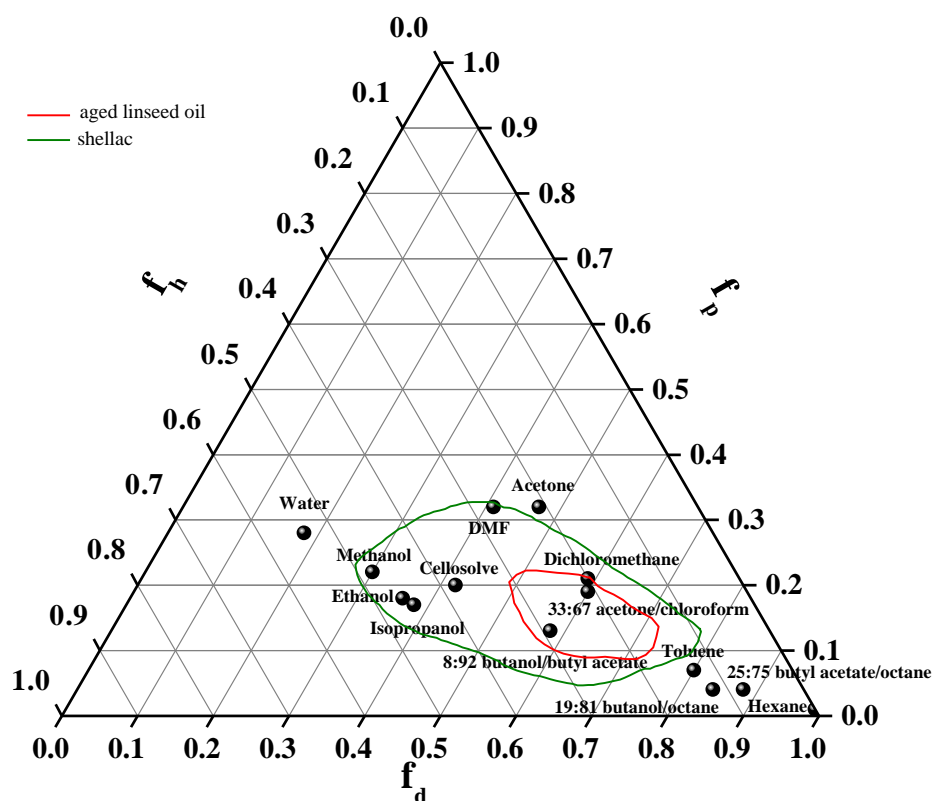

Figure 4.1: Teas chart of 10 solvents with solubility windows of shellac and linseed oil, along with solubility parameters for 10 common conservation solvents, and room temperature azeotrope mixtures.

As can be seen in Figure 4.1, the solubility windows for shellac and linseed oil are shown, along with four azeotropes taken from coatings literature: 33:67 vol% acetone in chloroform , 8:92 vol% butanol in butyl acetate, 19:81 vol% butanol in octane, and 25:75 vol% butyl acetate in octane (55). Two of the azeotropes plotted, 8:92 vol% butanol in butyl acetate and 33:67 vol% acetone in chloroform, would not be useful in shellac removal since they lie in the maximum swelling region for oil paint. In contrast, while the other two azeotropes plotted, 19:81 vol% butanol in octane and 25:75 vol% butyl acetate in octane, lie outside of the solubility window for linseed oil, they also fall far enough away from the solubility window of shellac to not be useful. They would likely be even less effective at removing shellac than the purported azeotrope or the true azeotrope of isopropanol and hexane. Unfortunately, these azeotropes given in the coatings literature would not be useful in the removal of shellac, but with further research, other room temperature azeotropes that would be useful for varnish and overpaint removal in art conservation could be determined.

The results from analysis of the 9.5 vol% isopropanol in n-hexane solution showed its room temperature azeotropic behavior. However, introduction of the azeotrope onto the surface of a representative oil paint film disrupted the composition by preferentially adsorbing isopropanol, as indicated by a loss of this solvent component in the headspace over the paint film. This is problematic because it indicates that there is some interaction occurring between the oil paint and the azeotrope, questioning the usefulness of even this solvent mixture for maintaining constant composition during a cleaning treatment. The extent to which this could damage or affect an oil painting is currently unknown, and further analysis of this composition in the presence of an oil paint film over the course of

its evaporation is needed. Analysis of the azeotrope's behavior on an actual oil painting would also be beneficial as it would provide a better idea of what interactions occur when the sample contains additional resins, varnishes, oil medium, and other additives. At this point, conservators should be wary of the use of boiling point azeotropic solutions since they are unlikely to behave as expected under room temperature evaporation conditions. True room temperature azeotropes should be determined experimentally prior to use, however even these cleaning solutions are liable to behave as zeotropes when contacting the highly unpredictable components of traditional oil painting.

4.1 Forensic Applications

Azeotropes are useful as cleaning solutions for oil paintings in conservation, but also have potential to be useful in the extraction of analytes in forensic samples. Due to their ability to evaporate with constant composition and be selectively chosen based on solubility parameters of the desired substrates through the use of Teas charts, azeotropes could be used to extract specific analytes from forensic samples such as explosive debris and illegal drugs. These types of forensic evidence require great care during collection and can prove to be a challenge since they are fragile and susceptible to contamination or degradation. The analysis of the evidence continues to present even more challenges since extensive sample preparation is often required before analysis can be completed. Solvents similar to those studied in this project, isopropanol and n-hexane, are used to wash explosive residue from debris or to extract controlled substances from complex illegal drug powder samples that often contain cutting agents (63-65). The type of

analysis and methodology used in this project are similar to those used in the analysis of many types of forensic evidence, specifically explosive debris and illegal drugs.

In the analysis of explosive debris, there are several types of sampling methods that can be used on areas that explosive residues have the potential to persist. One of the most common methods is swabbing and it is done with the use of cotton swabs to collect residue from non-porous surfaces suspected to have explosive residue (66). Some of the analytes desired for extraction from this residue include 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), nitrocellulose, and nitroglycerin. The ability of cotton swabs to collect explosive residue from debris is largely dependent on the swabbing solvent selected. A variety of organic solvents can be used since many explosives are easily dissolved in these solvents, such as ethanol, isopropanol, and acetone (66).

However, these solvents can sometimes have detrimental effects on the evidence since they are harsh and may dissolve unwanted analytes, similar to how some solvents suitable of cleaning oil paintings of their varnish and resin can also disturb and dissolve the oil paint underneath. In addition to the desired explosive residue to be dissolved with the swabbing solvent, a variety of other unwanted materials can be dissolved, such as plastics and coated surfaces, and subsequently interfere with instrumental analysis (66). For example, while dichloromethane (DCM) is a good solvent to use to dissolve nitroglycerin, it also dissolves polyvinylchloride (PVC), which is a compound that is undesirable in the analysis of explosive residue.

Explosive devices are often constructed using PVC pipes, so an ideal swabbing solvent that dissolves the desired explosive residues would not dissolve any of the PVC,

which would minimize contamination and interference. A solvent could be chosen to selectively dissolve explosive residue from PVC pipes with the use of a Teas chart. The fractional solubility parameters for the same ten solvents commonly used in conservation are shown on the Teas chart below (Figure 4.1), since some are also used in the extraction of analytes from explosive residue (66). The solubility windows for PVC (red) and cellulose nitrate, also known as nitrocellulose (green), are also shown. The solubility parameters plotted for TNT and nitroglycerin, also seen in Figure 4.1, were calculated as fractional parameters based on the Hansen solubility parameters (67). As shown in Figure 4.1, dichloromethane proves to be a good solvent for the extraction of nitrocellulose, since it falls well within the estimated solubility window for this compound, but it also falls on the estimated boundary of the solubility window for PVC. The data shown in the Teas chart confirms that acetone is a good solvent for the extraction of nitrocellulose since acetone falls within the solubility window approximated for nitrocellulose. It also shows to be an ideal solvent for this purpose since it does not dissolve PVC. However, nitroglycerin falls within the solubility window of nitrocellulose, so solvents need to be carefully selected in order to separately extract these analytes. It can be noted that the solubility windows for PVC and nitrocellulose as well as the solubility parameters for TNT and nitroglycerin are estimates approximated from the limited solubility data available. Further research should be done to provide more solubility parameter data that could be used to plot more informative solubility windows for each of the analytes included.
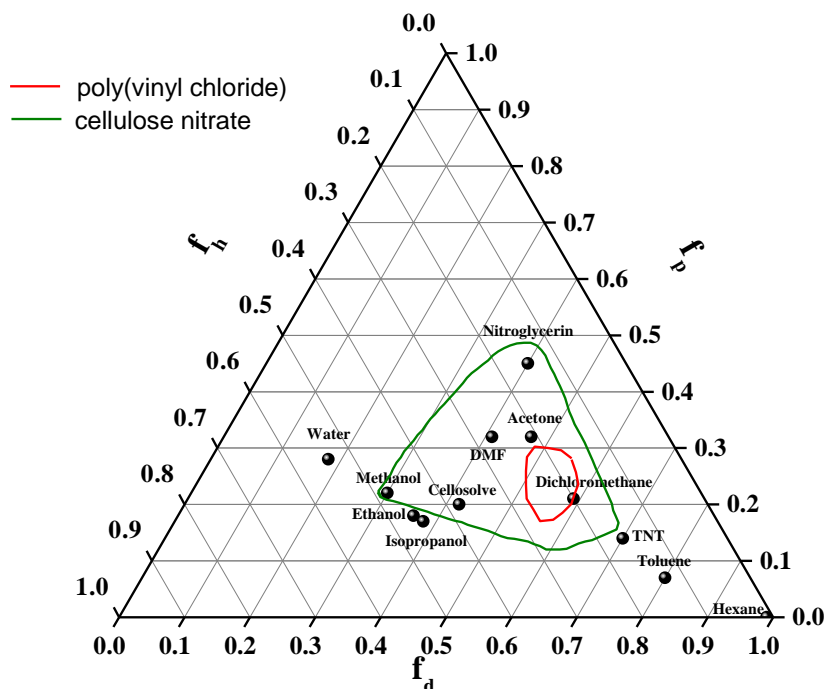
Figure 4.2: Teas chart of 10 solvents with solubility windows of PVC and nitrocellulose, and solubility parameters for TNT and nitroglycerin.

In addition to use with explosive residues, solubility theory could be of great use in the extraction of controlled substances from samples. Typically, many seized illegal drug samples contain much more than just the controlled substance, typically in the form of cutting agents. These cutting agents include diluents and adulterants that are added to the drug. Diluents are inactive additives, or "thinners," that are intended to increase the size of the drug sample and its supply for use. Adulterants are active ingredients that can be added that have effects similar to those of the intended drug, and are usually used together with the drug (63-65). These added cutting agents complicate the analysis of controlled substances, so the goal for forensic scientists is to extract the controlled

substances with solvents that do not dissolve the additives. Heroin, cocaine, and amphetamine are among some of the most common controlled substances analyzed in forensic laboratories that could benefit from selective extraction using solvent theory and Teas charts. Typically a series of "dry" extraction techniques are used in order to separate out components of interest from a mixture containing many components. Dry extractions utilize organic solvents only, not including water, in order to dissolve out a specific component that is more soluble in a certain solvent than the other components in the mixture. However, these dry extractions can be time consuming since a single dry extraction can only be done in one step if only one component is desired to be isolated from a mixture, and not multiple components. In order for dry extractions to be successful there also has to be great enough difference in the solubility of the component of interest and the diluents in the mixture, on the order of 10-100 fold (63-65).

One example of a controlled substance that is separated from a mixture by dry extraction is cocaine. Cocaine is also an example of a drug that can be found in either its hydrochloride (HCl) salt form or its base form. The form that the cocaine is in not only makes a difference when it comes to using dry extractions, but also when it comes to determining the amount of controlled substance present for Federal sentencing purposes (63-65). In order to properly and correctly determine the salt form, the dry extraction scheme has to be efficiently designed. This is where the solubility data for various solvents available for each of the components in a mixture in addition to cocaine is important. The solubility of cocaine base and cocaine HCl varies for most solvents used for dry extraction. For example, chloroform is a good solvent to use to extract cocaine base, as it is very soluble in this organic solvent. However, cocaine HCl is only freely

soluble in chloroform. In addition, a variety of diluents that are typically found in a mixture with cocaine, including starch, sugars, and baking soda, are insoluble in chloroform. In this case, a single extraction could isolate the cocaine in either form from a mixture containing these components (63-65).

This is not always the case with cocaine samples though, since adulterants are usually components in the mixture as well. Adulterants typically found in cocaine samples include nicotinamide, acetaminophen, lidocaine HCl, procaine HCl, and benzocaine. In a sample mixture containing cocaine HCl and all of the adulterants listed above, as well as the diluents that were mentioned previously, several dry extractions would need to be done. The first dry extraction with the use of acetone would extract lidocaine HCl, acetaminophen, and nicotinamide without dissolving the cocaine HCl. A second dry extraction with ether would need to be done in order to extract the benzocaine. Chloroform could then be used as a third dry extraction solvent to extract the cocaine HCl out of the mixture, since procaine HCl and the remaining diluents are only slightly soluble and insoluble in chloroform, respectively (63-65). While this is an effective and successful method used to extract components out of drug samples, multiple dry extraction steps can be time consuming and complicate the forensic analysis if the extractions don't completely dissolve all of the unwanted components from a mixture.

As was discussed previously with the application of explosive residues, Teas charts could prove to be a useful tool in determining solvent mixtures to use in the dry extractions of controlled substances. Each of the previously mentioned controlled substances has varying solubility information for the various solvents that can be used to extract them from complex illegal drug samples. These different solvents could be

plotted together as solvent blends in order to find mixtures that are suitable for extracting

multiple components out of drug samples that could eliminate so many dry extraction

steps. For example, solvent mixtures that have solubility parameters similar to ether and

acetone could be plotted to see what is capable for extracting out multiple adulterants.

The same could be done to plot solvent blends similar to chloroform in order to extract

out cocaine HCl, but no other diluents or adulterants. In order to determine which

solvent blends would then be appropriate for the extraction of specific components, the

solubility data for controlled substances could be plotted as regions on the Teas chart, as

was done with certain explosive residues. However, the necessary solubility data

currently available for controlled substances is limited, and can only provide an

approximate location of the solubility parameter on a Teas chart. Further research could

provide the additional solubility parameters necessary to plot solubility windows, and

help to determine which solvents to use to selectively dissolve the controlled substances

from the cutting agents and other additives.

Another benefit to using solubility theory in the extraction of explosive residues and

controlled substances is the potential to determine room temperature azeotropes capable

of dissolving the explosive residue and controlled substance analytes, as discussed

previously. Choosing an azeotropic mixture based on the solubility parameters of its

solvent components would be ideal for this application since the solvents can be selected

based on what analytes are desired to be dissolved. From gathering additional solubility

data, azeotropic mixtures could be chosen from lists of given binary mixtures, which can

be found in the CRC Handbook of Chemistry and Physics, based on their selective

solubility and location on the Teas chart in relation to compounds to dissolve. Binary

solvent mixtures of acetonitrile and dichloromethane are stated as being used in one application with the extraction of explosive residue from soil (68). These two solvents are not listed as forming an azeotrope in the CRC Handbook or other literature; however, they have proven to be a useful mixture in the extraction of various explosives with a nitro-group.

An additional benefit with using azeotropes in the extraction of analytes from explosive residues and controlled substances is that they have the potential to greatly increase sample size. This is due to azeotropes having a higher vapor pressure and as a result, can evaporate more quickly. Having a higher vapor pressure and quicker evaporation rate, azeotropes would be able to increase the amount of sample in a headspace vial that would totally vaporize. The vapor pressure of a liquid is temperature-dependent and is the pressure exerted by a gas in equilibrium with the liquid in a closed container (46). In principle, the lower the boiling point of the solvent used for extraction, the more sample that can be vaporized and introduced. This is due to the relationship between boiling point and vapor pressure, which governs the idea of total vaporization of solvents. If a greater amount of solvent could be added and vaporized, in turn a higher concentration of the analyte could be analyzed and detected. Total vaporization is a technique of great interest to the Goodpaster laboratory, and employed in the analysis of explosive residues. Further research into this application of azeotropes could provide valuable information and the potential for better detection limits of explosive residues.

Azeotropes would be of great use not only in the extraction of analytes from explosive residues, as they would increase the sample size able to be analyzed in addition to having the ability to be selectively chosen based on solubility parameters of the

explosive residue, but also in the extraction of controlled substances from illegal drugs. Solvent azeotropes have already been shown to be useful in the cleaning and removal of varnish from oil paintings, and have potential to be useful in forensic applications as well. Azeotropes and their application through the use of solubility parameters and Teas charts have a promising future in forensics. With further research into the solubility parameters of analytes in typical forensic evidence, this common tool used in conservation studios could soon become a valuable tool used in forensic laboratories.

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