The Organic Analysis of Artworks:
Early Challenges and Future Directions

In learning from our own past, we can look towards new areas of research as well as areas that are in need of revisiting. During a group discussion on the role of science in art conservation, David Bomford, newly appointed Director of Conservation at the Museum of Fine Arts in Houston, shared his sentiments regarding the future direction of collaborative research:

> In terms of traditional analysis of works of art, with old master paintings, pigments have been the most important thing- but that's because pigments are what we can analyze most straightforwardly. Actually, the medium is equally important but much more difficult to analyze. It's only been in relatively recent times that we've had successful and reliable medium analysis. There's still an awful lot about medium analysis we don't understand. I think there are analytical techniques that we are not yet capable of doing that will yield important information (Drayman-Weisser et al. 2010, 22-3).

The increased sensitivity of today's instruments and our more complete understanding of the complexities of materials analysis have revealed that we may need to re-examine certain areas of conservation science. Pigment interactions with organic binders, the analysis of complex mixtures, detection limits, and the comparison of analytical protocols and instrumentation are some of the more important subjects requiring our attention. In the twenty-first century such topics warrant closer inspection from scientists and conservators who are working in tandem.

Conservation science has unique complicating factors that do not plague other scientific fields. Some scientists working in academia or in industry tend to avoid consulting references that are over a decade old. Often there is more than one laboratory attempting to answer the same question, allowing scientists to build upon the work of their colleagues. Experiments performed 10 or 15 years ago may use technology or analytical protocols that have since become irrelevant or outdated.

This approach, however, would be devastating for the conservation community. Such a constraint would limit the literature that could be reliably cited to a small fraction. While students and practicing professionals should not be discouraged from consulting older references, they should try to surmise how a similar research project or experiment would be performed today. An awareness of our instrumental limitations, past and present, will better inform us as we move ahead.

The evolution of detectors and camera systems used for Infrared Reflectography is a perfect example. There are many paintings where no underdrawing could be discovered using the older silicon CCD detector (approx. 750-1050 nm) technology; this may have led some to the erroneous conclusion that a particular painting did not possess such features. However, beautiful, crisp preliminary underdrawings can now be captured using more current systems such as an InSb detector. These are capable of a much wider range (approx. 1000-3000 nm) and at a far higher resolution.

IRR systems have evolved, as have other analytical instruments, particularly those used to answer questions relating to organic materials thus increasing our knowledge bank of past materials. There are a handful of books and articles that outline this progression in conservation science.

The Getty's 1999 publication *Infrared Spectroscopy in Conservation Science* provides a thorough historical summary of the technology beginning as early as 1800 in the first chapter. This small section presents the average reader with the background, context and, more importantly, when and how the technology was introduced to the field of conservation.

Another example is the analytical section in the soon to be published *Conservation of Easel Paintings* edited by Dr. Joyce Hill Stoner and Rebecca Rushfield. This text incorporates an account of the entire history of various technologies including X-Ray analysis (XRF, XRD, SEM-EDS, etc), chromatographic analysis (e.g. GC, LC), FTIR, and analytical methods that are newer to our field (e.g. SIMS, MALDI). Dr. Jilleen Nadolny's section traces the relationship between art conservation and the sciences beginning as early as 1780. The following chapter, co-authored by conservation scientists Dr. Joyce Townsend and Dr. Jaap Boon, places every instrumental method into context, explaining how each relates to the history of paint analysis.

The book *The Organic Chemistry of Museum Objects* written by pioneering scientists Dr. Raymond White and Dr. John S. Mills, first published in 1987, has served as a seminal textbook in conservation laboratories and graduate programs throughout the world. Mills and White were the first to apply chromatography coupled with mass spectrometry to the vast and complicated world of art materials.

Their second chapter provides a comprehensive overview of several chromatographic methods including thin-layer (TLC), gas-liquid (GLC or GC), pyrolysis (Pyro-GC), and high performance liquid chromatography (HPLC). Many of the challenges and ambiguities that plagued Mills and White throughout their years of research, however, are less well known but help illustrate the challenges of early organic analysis.

Both scientists were initially limited to a rather simple gas chromatograph that was located in the bowels of the National Gallery in London. White's FAIC oral history interview provides an eye-opening account of his first impression of the laboratory. England's Secrets Act at the time had prevented him from visiting the government run facilities until he had officially accepted the position:

> […] and then I was taken on a tour of the laboratory and I was absolutely horrified, absolutely horrified because it was in the lower Duveen Rooms, what is now the big unloading bay. That was the main chem-

istry laboratory. This big huge cavernous area, with great high ceilings and, a vast area, and then the series of offices dotted round, and then the simply huge sort of hole like area which was piled up to sort of above your head with bits of government surplus and old bits of equipment that had been coupled in to make, you know, to make little research projects and so forth, these whole crates.

And, when I got to the chemistry laboratory I was just simply appalled because there was a gas chromatograph, quite a primitive gas chromatograph, a PAN gas chromatograph well dating from the early '60s and so forth. […]…if you could keep the old PAN gas chromatograph working and so forth, you know, in terms of leaks and some custom couplings and that weren't too sophisticated as they are now, that was one thing.

Then, we didn't really have proper integrators, so if you didn't, as a matter of experience and judgment get it about right then some of your peaks would sail off the paper and then you wouldn't be able to do the palmitate stearate and the azelate to palmitate ratios and so forth. So, it calls for very fine, there was a need for very fine judgment.

And, the most annoying and challenging things was we had an old Honeywell chart recorder and that was the only means of recording the data in those days, which had a sort of ink reservoir which regularly blocked up or just stopped running in the middle of the trace and so forth. So, it was an absolute nightmare, an absolute nightmare to ensure that you actually got the results for a run. And, John was absolutely superb at handling that machine, that beast (White 2009).

White expressed his wariness towards the early GC and attributed most of the early success with the PAN gas chromatograph to John S. Mills. It was not until two decades later that the National Gallery London would receive their first mass spectrometer, a Kratas MS-25. This was a major event, and it changed things immensely.

Mass spectrometers allow for specific ion/molecular identification instead of simply relying on measuring the time it takes for a material to pass through the column. MS techniques permit the identification of a range of molecules that differ in both size and class by assigning a characteristic mass/charge (m/z) ratio to each species. Eventually this will allow scientists to organize a database that is similar to the IRUG (Infrared and Raman User's Group) database used for FTIR spectra, aiding analysts in matching unknown samples with reference materials.

Even with the arrival of the new Mass Spectrometer, Mills and White were still faced with challenges. Any impurities present in the sample or other unforeseen issues (leaks, column bleed, etc) would result in a compromised gas chromatograph, an issue that still plagues modern day scientists:

[The MS] was integrated with a Perkin Elmer gas chromatograph. It wasn't by any means a perfect machine, because the weakness was the actual interface between the GC and the mass spec. In those days, it was a real problem finding couplings that would, you know, would not leak and would be able to withstand vacuum and varying, you know, high temperature and so forth.

Unfortunately, it used silicone, a silicone silica mastic composition for the jointing between the lining from the GC into the…and then it had a sort of molecular separator to pump off the gas and so forth. And, that was always, that was a little bit of a weak, a weakness of the system. Because we started, then started doing work on triterpenoids, and of course, one needed the interface at quite a high temperature and we used to run it at about 280, something like that.

And, unfortunately silicone Poly Mount tends to gradually break down and so one was constantly having to remake and reseal the system. So, it was quite a nightmare keeping that system working. But, when it did work it worked very well (White 2009).

White's interview reveals a candid attitude in discussing what was successful and what was not. White also discussed his reservations with Thin Layer Chromatography: he stated "TLC really wasn't of any great use and sometimes gave sort of falsely possible things"(White 2009). Such candor is rare in conservation literature. The resultant data from a failed experiment may be as important to the field as a successful one. Perceived failures may prevent others from wasting precious samples trying to perform similar tests.

There are few detailed descriptions of sample preparation in conservation literature in contrast to articles found in scientific journals. This topic is tricky and complicated and may explain why Mills and White chose to limit this section to only three paragraphs in their book. Samples can be subjected to specific solvents or mixtures of solvents, periods of heating, anoxic conditions, and finally a specific chemical reagent, often referred to as the "derivatizing" agent. These compounds, of which there are dozens, can be used to chemically alter classes of molecules that exist in the sample (e.g. lipids, resins, proteins, etc) facilitating separation as well as recognition during analysis.

While this may sound like a simple, straightforward process, this is hardly the case. For example, exchanging one derivatization agent with another or performing a reaction in the presence of oxygen can significantly alter the final results, making some protocols more successful than others. As our instrumentation continues to become more complicated so too do our options for sample preparation and manipulation.

Although these multiple parameters may seem daunting, they should not discourage conservators from pursuing questions relating to organic analysis. Conservation scientists have been working to come up with very specific (and often elaborate) protocols that are tailored to meet conservators' needs. Two examples are shown in Figures 1 and 2 (Colombini et al. 2010, 718; Sutherland 2007). The drastic difference between the two methods is immediately apparent.

Figure 1. The flow chart picured below represents a sample preparation protocol developed by conservation scientist Michael Schilling at the Getty Conservation Institute. Prior to subjecting the sample to analysis using GC-MS, the analyst can choose between two different extraction methods to look for a) fatty acids, or b) fatty acids, proteins, and glycerol.
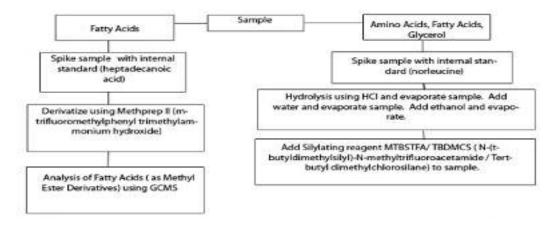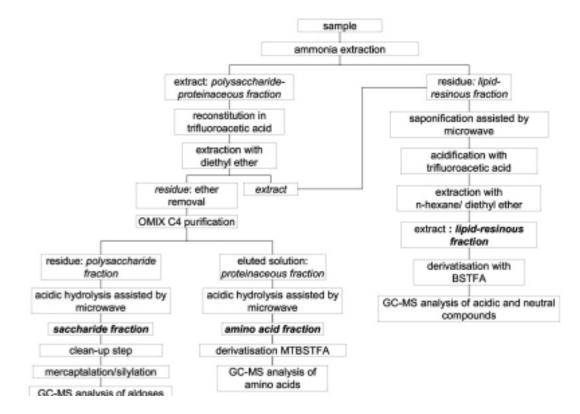

Figure 2. The flow chart below illustrates a protocol developed by scientist Dr. Maria Perla Colombini at the University of Pisa. This complicated protocol is designed to extract faty acids, resins, waxes, amino acids, and polysaacharides from a single sample. One drawback to using more elaborate extraction methods is the size of the sample. Larger samples are often required for extensive protocols when preparing for analysis using GC-MS.

Not every conservation science laboratory employs the same protocol or even has the same instrumentation. Scientists have recently come up with an efficient way of evaluating individual approaches to the analysis of artworks. In a "round robin exercise," one laboratory prepares a sample (or samples) that will serve as the unknown ("blind sample"). The blind sample is consequently sent out to a number of different conservation science laboratories and participants are asked to report back with what they are able to find.

Results from one of these "round robin exercises," as they are called, were recently published in 2011 and revealed some interesting findings (Colombini et al. 2011). In Figure 3 all eleven laboratories reported slightly different results, with some identifying components that were not actually present in the sample, which was for a 17th-century medical ointment (Colombini 2011, 1858).

Work is still needed to assess and compare various protocols and analytical approaches. This is precisely where conservators can offer their service and expertise. There are so many variables to consider, and scientists have little time to devote to preference sample preparation.

As instruments have become more sophisticated, we can no longer simply rely on generic reference materials. In the case of easel paintings, for example, one must take into account interactions between substrates, ground layers, pigments, surface coatings, and any restoration materials. While references will never serve as accurate substitutes for samples collected from actual artworks, questions regarding organic materials must still be placed into context. Modern materials may not really resemble the historical product

even if they are chemically similar. For example, 18th-century lead white is very different morphologically from the 20th-century version despite being of a similar chemical makeup.

Dr. Leslie Carlyle, now the Head of Conservation at the Tate, was one of the first to emphasize the importance of using historically accurate art materials for scientific research. Nearly a decade ago, Carlyle began the HART project (Historically Accurate Reconstructions Techniques), one of the most comprehensive projects involving artists' materials and recipes to date (The HART Project 2005). Her research has inspired others to re-evaluate older notions relating to reference materials. If the primary objective is to study the nature of the drying oil, simply painting out oils on glass slides is not enough. Artificial and natural aging is also important to consider as aged samples often exhibit different chemical and physical properties than freshly prepared materials.

On the other hand reconstructions still provide the best means to test current theories and the limits of our scientific instruments. One interesting example is the relatively recent "debunking" of the copper-resinate myth, specifically the preparation of the pigment. Artworks possessing copper-containing green glazes were analyzed and found to be devoid of individual pigment particles. Early scholars believed that these copper glazes were made by dissolving verdigris in heated resin or a resin-oil varnish. Reconstructions of verdigris paints, however, showed that even without heating, the copper pigments would react with the surrounding binding medium and eventually turn into a transparent layer lacking discrete pigment particles (Van Eikema Hommes 2005).

Figure 3. Pictured below is a chart summarizing the results obtained from a round robin exercise conducted in 2011. Eleven conservation laboratories were asked to identify the components in a blind sample that consisted of silver litharge, pig suet, olive oil, galbanum, beeswax, pine resin, and colophony. These ingredients were combined to reconstruct a 17th-century recipe for a medical ointment.

Laboratory	Analytical technique	Identified or hypothesised materials
1	FTIR	Plant oil (olive oil), beeswax, aromatic compounds
2	FTIR, XRF	Plant oil, beeswax, aromatic natural resin, $PbCO_3$
3	Micro-Raman, SERS	Animal fat, (pig suet), colophony or pine resin, galbanum resin, PbO (litharge and massicot), $PbCO_3$
4	NMR, HPLC-APCI-MS	Plant oil (*almond* or olive oil), animal fat, beeswax, Pinaceae resin, galbanum resin, *wine*
5	Py-GC-MS	Plant oil, beeswax, diterpenoid resin
6	GC-MS, SPME-GC/MS	Animal fat (pig lard), beeswax, *Pinus sylvestris* resin, *triterpenoid compounds*
7	GC/MS	Plant oil, animal fat, beeswax, Pinaceae resin
8	GC/MS, FTIR	Plant oil, beeswax, Pinaceae resin, $PbCO_3$
9	GC/MS, micro-Raman	Plant oil (*almond* or olive oil), animal fat, beeswax, Pinaceae resin, $PbCO_3$
10	GC/MS, HPLC-Q-ToF MS, FTIR, micro-Raman	Plant oil, beeswax, diterpenoid resin, PbO
11	HPLC-ESI-HR Tof MS	Plant oil (olive oil), beeswax, Pinaceae resin, *sandarac resin*

Materials not present in the unknown ointment are in italics

A second example demonstrating the important role of reconstructions involves a project carried out at the Tate Britain. A primary goal of the study was to identify copal resin in a number of well-documented Pre-Raphaelite paintings. Copal was a common 19th-century paint and varnish additive and was frequently used by painters belonging to the Pre-Raphaelite Brotherhood (Townsend et al. 2004, 47-8).

However, few of the samples collected from this group of paintings produced results that conclusively confirmed the presence of copal (Townsend et al. 2004, 62-7). This can be attributed to a number of factors including insufficient sample size and pigment interference. Fortunately Dr. Leslie Carlyle created a number of paint outs, reconstructing techniques and recipes used by these 19th- century artists. The very high refractive index of these copal-containing reconstructions closely matched the refractive index of samples taken for the actual paintings corroborating the use of copal resin (Townsend et al. 2004, 77-8).

The reconstructed paint references may be useful in answering future questions such as testing the detection limits of commonly used analytical instruments. Such a study would help investigate why copal was not successfully identified in the samples taken from the paintings. Analytical protocols used for the identification of binding media can only be improved when such limitations are explored.

A modern counterpart to Mills and White's seminal textbook did not appear until fairly recently. In 2009, Dr. Maria Perla Colombini and her Italian colleagues published a text that is nearly three times the length of Mills and White's *The Organic Chemistry of Museum Objects*, a physical testament to the exponential growth in scientific advancements that has occurred since 1987. Colombini's book has much to offer conservators.

The book's title, *Organic Mass Spectrometry in Art and Archaeology*, reflects the fact that by the 21st-century MS techniques had become the standard method used in the organic analysis of art objects. The book is organized by individual analytical techniques; each chapter includes an exhaustive bibliography and relevant case studies that may be of great interest to conservators. Colombini also delves into important topics such as derivatizing agents and detection limits.

Finally, Colombini and her colleagues do not hesitate to point out the dangers of relying too heavily on certain concepts, concepts that are based on the work of early pioneers such Mills and White. The reliance on fatty acid ratios for the identification of oils and proteins is a perfect example.

Scientists at the National Gallery in London have recently found that these ratios can be altered by the presence of certain reactive pigments (Higgitt et al. 2005). Colombini's team has also stressed that complicated mixtures (e.g. egg yolk mixed with drying oils), contamination from restoration materials, and even environmental factors can produce results that are misleading, resulting in misattribution (Colombini et al. 2010, 723). The various methods of refining oils such as water-washing, sun bleaching, and heating can also alter fatty acid ratios and while some laboratories have made considerable efforts to explore such relationships there is still much that remains to be explored.

Lastly, it may be worthwhile to mention the application of chemometrics to cultural heritage studies. Although archaeological conservators and conservation scientists may be familiar with chemometrics (also referred to as multivariate analysis or MVA), this term is relatively new to most practicing conservators.

The growing sophistication of non-destructive analytical techniques such as hyperspectral imaging, reflectance FTIR, and XRF can perhaps explain why MVA is now appearing more often in studies associated with conservation science. Such techniques combine statistics and complicated algorithms with computer programs, helping analysts to sift through large amounts of data in order to identify trends and patterns. As instruments become more sensitive and robust, conservators and scientists will continue to face exhaustive amounts of data.
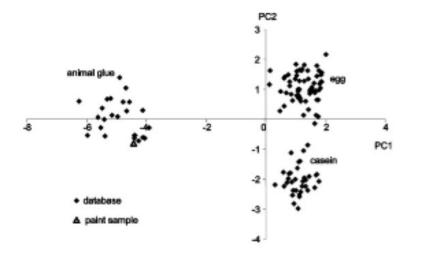

Figure 4. Pictured at left is an example of a plot generated using Principal Component Analysis (PCA). The plot depicts the relative amino acid percentages of glue, egg, and casein containing paint samples (non-aged and UV aged). Samples of unknown composition can now be compared to the cluster groups obtained using the PCA plot, assisting with the identification of proteinaceous materials in painted works of art.

In the last decade or so, computer programs have been designed to automatically perform MVA techniques, alleviating scientists and mathematicians from the burden of executing lengthy statistical computations. These programs can extract meaningful information from complicated datasets, revealing relationships that were previously unrecognized and assisting with identification and classification.

With all that is demanded of conservators, it may be too much to ask that we add such a complicated skill to an already over-sized list. Since the year 2000 there has been an exponential increase in the use of MVA techniques in the literature, specifically principal component analysis (PCA), an example of which can be seen in Figure 4 (Colombini 2010, 715).

Until conservation professionals develop an awareness of these methods, it will be increasingly difficult for some to comprehend some of these journal articles and thus exploit some of the benefits that MVA can offer.

Understanding the evolution of conservation science can help to better inform our research abilities and also foster a greater respect for our early pioneers in the conservation field. Their stories should provide inspiration for future conservation professionals even as technology continues to progress. Einstein urged people to "learn from yesterday" while at the same reminding us "not to stop questioning" (Darbellay et al. 2008, xix).

Like other fields that are closely tied to the sciences, the conservation field should also adhere to these tenants. By working together, scientists and conservators have been able to overcome past obstacles in an effort to bring new information to the conservation community, to scholars, and to other art enthusiasts. The formation of scientific databases devoted to art materials and the production of comprehensive publications prove that conservation professionals have surmounted some of the challenges posed by an ongoing technological revolution.

The analysis of organic materials, however, continues to test our limits. Collaboration among scientists and conservators is a prerequisite if we are to ever develop a comprehensive understanding of organic materials that are encountered in artworks and cultural heritage sites.

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