Beyond the basics: A systematic approach for comprehensive analysis of organic materials in Asian lacquers

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Identification of organic materials in Asian lacquers presents many challenges due to their complex formulations and the limited solubility of the main component, which is catechol-rich sap from three species of Anacardiaceae trees that crosslinks to form a hard film. Pyrolysis-gas chromatography–mass spectrometry with thermally assisted hydrolysis and methylation using tetramethylammonium hydroxide (THM-Py-GC–MS) has been shown to produce a wide range of marker compounds useful for identifying the catechol components and lacquer additives such as drying oils, natural resins, proteins, starch, and colorants. However, interpreting the test results is quite challenging because of the sheer number of compounds produced by pyrolysis and the wide range of materials that have been used in traditional Asian lacquer formulations. An expert system developed by scientists at the Getty Conservation Institute and conservators at the J. Paul Getty Museum for a workshop entitled ‘Recent Advances In Characterizing Asian Lacquers’ (RAdICAL) utilizes software tools to overcome challenges in data analysis and marker compound interpretation, making it possible for even relative newcomers to Py-GC–MS to identify materials in lacquered objects systematically. Automated Mass spectral Deconvolution and Identification System (AMDIS), a freeware program developed by the National Institute of Standards and Technology (NIST), systematizes GC–MS data analysis by rapidly deconvoluting chromatograms, identifying individual peaks, and then searching the results against a user library of marker compounds, producing a simple report that lists the names, retention indices, and peak areas for all the compounds identified in the sample. The authors have produced a custom RAdICAL compound library, compiled from in-house studies of reference samples made from mixtures of raw or processed lacquer mixed with additives, and supplemented by published work from other researchers. The lists include numerous oxidation products of the alkyl- and alkenyl-substituted catechols, and alkyl- and alkenyl-substituted benzenes in the tree saps identified in studies of aged lacquer replicas, many of which have diagnostic purposes. A specialized Excel workbook developed for RAdICAL can import the AMDIS report, organize the marker compound results by class of artists’ materials, and perform automatic calculations to display sorted information for each material in specialized diagnostic graphs. Expert knowledge relating raw materials to their associated marker compounds, obtained from in-house research, publications and personal communications has been embedded into the individual Excel worksheets. This aids users of the workbook in verifying the presence or absence of materials in their lacquer samples, based on the marker compound distributions. All of the final results are presented in a pre-formatted comprehensive analytical report. Extensive lists of analytical data for marker compounds from the major classes of organic additives used in Asian lacquer formulations provide researchers the information needed to identify these markers in unknown lacquer samples. As other researchers contribute marker compound information for further lacquer materials and the knowledge for interpreting them, the capabilities of the RAdICAL expert system will continue to expand.

Keywords: Anacardiaceae, AMDIS, Arlenic acid, Asian lacquer, Gestalt graph, Mazzeic acid, Pyrolysis-gas chromatography–mass spectrometry, RAdICAL, Thermally assisted hydrolysis and methylation, Thitsi, Urushi

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Introduction

Currently, pyrolysis-gas chromatography–mass spectrometry with thermally assisted hydrolysis and methylation (THM-Py-GC–MS) is the best analytical technique for characterizing the full range of organic materials present in Asian lacquers. It provides the most detailed compositional information about the catechol-rich saps from the three main species of trees in the Anacardiaceae family used in Asian lacquers (abbreviated to Anacards), as well as a wide range of lacquer additives. Although the analysis itself is easy to conduct, Py-GC–MS data evaluation can be quite challenging, especially for newcomers to the technique. The key difficulty in data evaluation is recognizing the connection between artists’ materials present in the lacquer sample and the sets of associated marker compounds formed by pyrolysis of these materials in the presence of tetramethylammonium hydroxide (TMAH).

An expert system developed by scientists at the Getty Conservation Institute (GCI) and conservators at the J. Paul Getty Museum (JPGM) to characterize organic materials in Asian lacquers overcomes many challenges of Py-GC–MS data interpretation. The two components in the expert system are:

1. Processing of the GC–MS data with Automated Mass spectral Deconvolution and Identification System (AMDIS) to identify marker compounds systematically and calculate peak areas;
2. evaluation using Excel to interpret and present peak area results comprehensively.

This article describes the expert system, provides complete tables of marker compounds for identification of artists’ materials used in Asian lacquer formulations, explains in some detail how software tools can be used to facilitate data analysis, and presents important graphs and tables used for data interpretation. It is intended to be a companion to the other articles in this supplement to Studies in Conservation. Marker compounds and information for identifying European lacquer materials are also in the system, but are beyond the scope of this article.

The expert system is one component of a GCI workshop entitled ‘Recent Advances In Characterizing Asian Lacquers’ (RAdICAL), in which sampling of lacquer layers by micro-excavation of flake samples and the use of histochemical stains for mapping organic materials in cross sections are the other two topics. RAdICAL provides a unique opportunity for scientists and conservators to work in close collaboration using analytical techniques to aid the understanding of lacquered objects in their institutions (Getty Conservation Institute, 2016). Venues for RAdICAL have included the GCI (2012), the Institute for Preservation of Cultural Heritage at Yale (2013) and the Centre for Research and Restoration of the Museums of France (2014).1

THM-Py-GC–MS analytical procedure

At the GCI, THM-Py-GC–MS analyses were performed on a Frontier PY-2020D microfurnace pyrolyzer interfaced to an Agilent 7890A GC/5975C inert MSD. Samples placed into 50 μl stainless steel Ecospher cups were treated with 3 μl of 25% TMAH in methanol and pyrolyzed at 550°C.2 A J&W DB-5MS-UI capillary column (30 m × 0.25 mm × 0.25 μm) attached to a Frontier Vent-Free adaptor was used (40 m effective column length), with the helium flow set to 1 ml per minute. The split injector was set to 320°C with a split ratio of 20:1. The oven of the GC was held at 40°C for two minutes then ramped to 320°C at 6°C per minute, followed by a nine-minute isothermal hold.

Use of this expert system will ensure that highly comparable results will be obtainable by analysts working with Py-GC–MS instrumentation from different manufacturers, thus maintaining reproducibility between laboratories.

Reference samples

Careful study of reference materials is, of course, critical to sophisticated interpretation of chromatograms. Only through such study can we characterize the full range of marker compounds produced by the wide variety of raw materials used in lacquer production. Over the course of the last decade, and in collaboration with generous collaborators, we have built a reference collection of various lacquer types including urushiol-, laccol- and thioisol-based lacquers from China, Japan, Korea, Taiwan, Thailand, Cambodia, and Burma. In Py-GC–MS, marker compounds for materials may vary with the sample matrix, so we have prepared standards made with a variety of additives mixed into Anacard lacquers, including a range of vegetable oils, natural resins, essential oils, protein-based materials, starchy materials, and natural dyes. Most of the standards were coated onto glass microscope slides in batches of four to five, and cured at approximately 80% relative humidity for several days. In some instances, standards were prepared on other substrates, such as wood or traditional ground materials. One

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1The appendices provide information, encourage readers to attend a RAdICAL workshop where they will receive training and copies of the Excel workbook and AMDIS library. Eventually, there are plans to write a book on RAdICAL that will contain all of this information.
2A limited study was carried out on the effects of pyrolysis temperature on the peak area results for THM-Py-GC–MS of Japanese roiro lacquer in order to ascertain the optimum pyrolysis temperature of Anacards in the presence of TMAH. The yields for selected marker compounds were measured for identical powder samples that were pyrolyzed at 400, 450, 500, and 550°C. Overall, the yield of Anacard markers relative to the oil content was reduced nearly by half, largely due to an almost complete loss of hydrocarbons, whereas no significant improvement was observed in the yield of acid catechols (an important set of marker compounds) compared to saturated catechols. Thus, there seems to be no advantage in using a pyrolysis temperature below 550°C for the identification of Anacards in lacquer samples.
example of each standard was then exposed to light in an east-facing window at the Getty Museum for up to two years; the remaining examples are kept in dark storage and are available for future study.

**Expert system for data processing**
AMDIS is a freeware program developed by the National Institute of Standards and Technology (NIST) that automates the process of identifying compounds in GC–MS sample data files by means of mass spectral library searching. Detailed explanations of how AMDIS processes data are available elsewhere (Stein, 1999), but a brief description will help explain its most powerful feature, deconvolution. When AMDIS is run on a data file for a sample, it scans the entire chromatogram and groups together (or extracts) into a single mass spectrum all those ions that rise and fall at the same retention time and which exhibit the same peak shape. This is obviously the case for ions originating from an eluted compound (which AMDIS terms a component). Conversely, ions exhibiting constant intensity over the same time period are excluded from the extracted mass spectrum for the component. Sources for such ions include siloxane compounds present in column bleed (component. Sources for such ions include siloxane compounds present in column bleed ($m/z$ 207, 281, and 355) and air in the helium carrier gas ($m/z$ 18, 28, 32, and 40). Consideration of peak shape in the deconvolution process leads to vast improvements in the quality and purity of the extracted mass spectra for partially co-eluting components when compared with manual background subtraction results. After compiling the entire set of component mass spectra in the GC–MS results, automated searching of each extracted mass spectrum against a user-generated library identifies compounds (termed targets) in the chromatogram and tabulates the search results. Users can scroll through the target compound list and review the accuracy of the library match results. The AMDIS report lists the library match factor and peak area for each target compound identified in the sample, plus a number of other evaluated results, sorted by retention time or retention index (RI) (if applicable). RI is a useful sorting parameter for most purposes because the target compound list relates directly to the peak order in the chromatogram. Typically, it takes less than a minute for AMDIS to process a data file, which is an enormous practical benefit of using the program for data analysis.

AMDIS version 2.70 bundled with the NIST MS library version 2.0 g was used in this study. Although AMDIS is also available for free download from the NIST website (NIST, 2016), one distinct advantage of the bundled version is the capability of performing NIST searches within AMDIS. For most lacquer samples, default program parameters for resolution, sensitivity and component width are adequate. RI may be used as a compound identification parameter in AMDIS analysis, which greatly improves the match accuracy for homologous series of target compounds, such as hydrocarbons, because the members tend to have similar mass spectra. Accordingly, RI-type analysis is recommended for lacquers. This feature requires that users first analyze a mixed hydrocarbon standard using the same GC–MS method in order to calibrate RI for the method. The AMDIS library developed in the Getty research, compiled from test results from numerous lacquer standards mixed with additives, contains mass spectra for more than 700 target compounds. Regarding library matching, users must specify a minimum match factor above which AMDIS will report spectral matches to library compounds. A value of 80% works well for RI-type analyses of lacquer, but for simple (non-RI) analyses of other sample types the value should be set higher.

As mentioned in the introduction, compound identification is only the first step in identifying materials with Py-GC–MS. A list of compounds present in the test result for a sample is not necessarily helpful to analysts who lack an in-depth understanding of the materials that form them, especially in complex materials such as lacquer. Typically, an expert level of understanding in lacquer analysis comes only after years of effort and practical Py-GC–MS experience, so that newcomers to the technique face a formidable knowledge barrier before attaining competence. Relevant publications by experts are useful for narrowing the knowledge gap, but comprehensive information is difficult to obtain because the lacquer literature is highly diverse, spread over many different publications and written in many languages. Marker compounds identified in publications may be difficult to locate in users’ chromatograms because retention indices are seldom published.

An innovative approach to Py-GC–MS data interpretation developed in our research utilizes expert knowledge integrated into a Microsoft Excel 2013 workbook to process target compound results from AMDIS reports for the purpose of identifying artists’ materials in lacquers. The workbook accepts the AMDIS report, sorts the target compound information, reorganizes it by class of material, and presents interpreted results with graphs and tables. Expert knowledge culled from scientific publications and from interviews with researchers experienced in lacquer materials provide marker compound lists for various lacquer materials and tools for interpreting the results.

One difficulty encountered in developing the workbook was identifying a field in the AMDIS report that could serve as a sorting parameter to make the target compound results fit into pre-formatted Excel worksheet templates. Each AMDIS library entry has
several fields into which users enter relevant data for the target compound: Chemical Abstracts Service number (CAS #), compound name, molecular formula, RI, notes, and an ion for calculating signal-to-noise ratio (termed ‘Ref. Ion’). Although a CAS number is itself an unambiguous descriptor for a chemical compound, it does not easily lend itself to sorting. Because signal-to-noise data were deemed unessential for our study, we decided to use this field (Ref. Ion) to assign a library entry number for each target compound in the RAdICAL library. The library entry number is simply a convenient way to allow our Excel workbook to search the list of target compounds reported by AMDIS quickly and match them with marker compounds in the RAdICAL library.

The RAdICAL Excel workbook contains multiple worksheets that handle specific tasks in the semi-automated data evaluation process. The AMDIS sample report is pasted into one worksheet, and the CSV file of the corresponding GC–MS chromatogram is pasted into a second. The target compound results in the AMDIS report are automatically processed by the lookup formula, extracted and reorganized in a separate ‘Material Verification’ worksheet in which all of the identified compounds are grouped according to their likely material of origin. In this worksheet, users decide whether or not that material is present in the sample based on the peak area, RI and library match factor data for each of the compounds identified in a given material.

To make this task easier, expert knowledge is provided. The ‘Interpretation Tools’ worksheet, giving users the information they need to verify if a representative number of marker compounds were detected. For example, 21 marker compounds found to be associated with pine resin are listed together in a single column in the ‘Material Verification’ worksheet. Expert information indicated that of these 21 compounds, methyl dehydroabietate (DHA), methyl 7-methoxy-tetradehydroabietate and methyl 7,15-dimethoxytetradehydroabietate must be present in a sample and the peak area results for a sample and verify the presence of aged pine resin is indeed present. If so, then users would choose to ‘verify’ pine resin as an identified artists’ material present in the sample, and the peak area results for the compound group will then be added together into the tables and charts that follow. If, on the other hand, these compounds are not present, the user chooses not to verify and the peak area results for any markers in the pine resin category will not be tallied.

After the user verifies the presence or absence of each of the classes of materials in the lacquer sample that are represented by the AMDIS library, the total peak area is calculated for each of the identified classes, and a pie chart presents the peak area percentage of each class of material that was detected in the sample. Peak areas are related to concentration by detector response factors, which can be obtained only through the use of calibration standards for every compound identified. Of course, this is an impossible task when dealing with complex, multi-component pyrograms from natural products such as Asian lacquer. Thus, the peak area pie charts are currently the best way of presenting overall composition of the sample. They are most useful for showing relative amounts of material classes in comparisons of test results for multiple samples taken from a single object. For example, an upper lacquer layer on an object might contain more Anacard sap and less oil than a lower lacquer layer from the sample object, or an upper lacquer layer might contain more urushi and less hitis than a lower lacquer layer. There is greater risk involved in comparing sample results between objects because of gross differences in the formulations.

The RAdICAL workbook developed at the Getty also contains worksheets that automatically produce pre-formatted report templates. This means that headers, tables, and graphs of results appear in the report as soon as the AMDIS report and CSV file are pasted in and the materials present in the sample are verified. The report templates include blank fields where the analyst’s comments and interpretations may be added. Many additional formulas used in the Excel workbook are beyond the scope of this article, especially in the area of graphing and automation.

In the subsequent sections of this article, examples of the processed data are presented for each class of artists’ material represented by marker compounds in the RAdICAL workbook. Graphs are important interpretive tools for identifying oils and Anacards, whereas for other materials, data tables are currently the most relevant format. Tables of selected marker compounds for the main material classes are presented in the Appendices. The term ‘unverified’ is used in the appendices to denote marker compounds that are reliably present in test results for a particular material but for which the molecular structure is unknown. The status of unverified markers may change in the future, depending on the outcomes of further research on the materials, and chemical structures may eventually be assigned to them. Each section contains specific expert knowledge needed to interpret the marker compound results for a sample and verify the presence of the materials.

**Drying oils**

The vast majority of oils and lipids are composed of glycerol esters of fatty acids. Appendix 1 lists four classes of marker compounds for oils and lipids: methyl esters of monocarboxylic and dicarboxylic...
fatty acids, methyl ether derivatives of glycerol and methyl alkylphenyl alkanoates (APAs), which are formed from highly unsaturated linolenic and oleostearic acids by bodying linseed, perilla or tung oils at elevated temperatures (Evershed, 2007). When interpreting sample results in the RADICAL workbook for markers associated with oils and other lipids, the presence of dicarboxylic and monocarboxylic fatty acids together is indicative of drying oils; for samples with significant oil content, glycerol may also be detected.

Generally, fatty acid peak area ratios developed originally for identifying oils in Western easel paintings (Mills, 1966) have been found to be applicable to Asian lacquer materials. For instance, because drying oils produce high levels of azelaic acid during the aging process, the A/P ratio (dimethyl azelate to methyl palmitate) broadly differentiates drying oils from other materials that contain fatty acids (semi- and non-drying oils or fats from egg, animal glue, blood, and raw Anacard lacquers). We have discovered that the ratio of APAs to monocarboxylic fatty acids reveals additional information about the heat-bodying conditions because the APA content increases with temperature. Another important ratio for lacquers is the total of fatty acids to glycerol. Raw Anacard lacquers contain measurable amounts of native fatty acids but little or no detectable glycerol, so fatty acid to glycerol ratios are reduced in samples containing raw lacquer mixed with triglyceride oils.

Mills discovered the dimethyl suberate to dimethyl azelate ratio (di-C₉/di-C₅) is elevated for bodied drying oils and low for cold-pressed drying oils in easel paintings (Mills, 1966), but comparable data for Anacard lacquers has yet to be compiled.

Table 1 lists information useful for interpreting test results for materials in Asian lacquer formulations that contain fatty acids. Four oils that produce high A/P ratios in lacquers are classified as drying oils. The ratio of P/S (methyl palmitate to methyl stearate) is used for oil identification. The unusually low P/S ratio of one makes tung oil from Vernicia fordii easy to differentiate from all other oils in lacquers. Partial overlap in P/S ranges makes it impossible to differentiate unambiguously between linseed oil, perilla oil, and tallow tree oil in samples. Chinese tallow tree oil is a drying oil also referred to as stillingia oil (from Sapindium Schiferum). Its excellent drying properties are attributed to high concentrations of 2,4-decadienoic acid and 8-hydroxy-5,6-octadienoic acid, which are unusual fatty acids that are not present in other oils (Chen et al., 1987). Because of difficulties in obtaining pure Chinese tallow tree oil in our research, we were unable to confirm the fatty acid compositions given in the references. Given its unusual fatty acid composition, it may be possible eventually to identify specific pyrolysate markers in lacquers made with this oil. Two non-drying oils are also associated with lacquer making. Rapa oil, also known as rapeseed oil, is used for cleaning lacquer brushes (Webb, 2000). Because it contains dodecanoic acid, dried films containing rapa oil have unusually high levels of undecanedioic acid relative to the other dicarboxylic fatty acids (van Keulen, 2014a). Sesame oil, which has a relatively low P/S ratio, is discussed in documents from the Northern Song Dynasty (Heginbotham et al., 2016). Obviously, more work needs to be done on testing botanically verified specimens of drying oils from Asia in order to define the statistical ranges of P/S more accurately and to look for additional marker compounds that might help differentiate oils.

It should be noted that ester-type waxes such as beeswax and carnauba wax, used in furniture polishes, contain significant amounts of fatty acids that may skew fatty acid ratios, making drying oil identification difficult at best. Additional markers include long-chain fatty alcohols (and their methyl ethers) and hydrocarbons (some of which will appear in graphs presented later in this article).

AMDIS peak area results for fatty acid methyl esters can be arranged by carbon number and plotted in a bar graph format, as shown in Figs. 1 and 2 for samples of red and black lacquer from a late-eighteenth-century Chinese carved lacquer screen in the collections of the Weltmuseum Wien in Vienna (Pitthard et al., 2016).

| Table 1 | Compositions of materials in Asian lacquers that contain fatty acids |
|---------|---------------------------------------------------------------|
| Product | P/S | Characteristic ratios and compounds |
| Tung oil | 1–1.2 | High A/P |
| Heat-bodied tung oil | 1–1.2 | High A/P; presence of APAs |
| Linseed | 1.2–2.5 | High A/P |
| Tallow tree oil | ∼3 | High A/P |
| Perilla oil | 2–4 | High A/P |
| Sesame oil | 1.5–2 | Low A/P |
| Rapa oil | 2–3 | Low A/P; presence of C22,1, C22, C20,1, C20, C24, monocarboxylic fatty acids; C11 dicarboxylic fatty |
| Blood | ∼2 | Low A/P; presence of blood markers and cholesterol |
| Urushi | ∼2 | Low A/P; presence of C15 Anacard markers |
| Animal glue | ∼4 | Low A/P; presence of glue markers |
| Laccol | ∼7 | Low A/P; presence of C17 Anacard markers |
| Thitsi | ∼7 | Low A/P; presence of C15 Anacard markers and alklyphenyl catechols |

*Ratio calculated from data by Jamieson and McKinney (1938) and Chen et al. (1987).*
The bar graph format shows the full range of fatty acid marker compounds and obvious differences in their prevalence between the samples; Table 2 lists the relevant ratios for these samples.

**Anacards**
Saps from lacquer-producing trees in the *Anacardiaceae* family are complex, water-in-oil emulsions consisting of substituted catechols, substituted...
phenols, carbohydrates, glycoproteins, and laccase enzyme (Kumanotani, 1995). Using Py-GC–MS, Miyakoshi and colleagues elucidated all the major pyrolytic pathways that lead to the formation of homologous series of marker compounds for Anacard lacquers: catechols, phenyl catechols, phenols, phenyl phenols, alkyl benzenes, and hydrocarbons. For each homologous series there is a maximum side chain length and a predominant member. For example, chromatograms of urushi (from Toxicodendron vernicifluum) show series of catechols, phenols, and hydrocarbons in which each has a maximum side chain length of 15 carbons and the most abundant member has seven carbons. For laccol (from Toxicodendron succedanea), the same series are present, but the maximum chain length is 17 carbon atoms and the most abundant member has nine carbons. The characteristic features of thitsi (from Gluta usitata or Gluta laccifera) are significant amounts of alkyl benzenes, with smaller amounts of phenyl catechols and phenyl phenols (Niimura et al., 1999; Niimura & Miyakoshi, 2000; Frade et al., 2009; Honda et al., 2010, 2015). These persistent Anacard markers have been detected in ancient Jōmon period lacquerware (Yuasa et al., 2015), Han dynasty burial objects (Khanjian et al., 2011) and ancient Chinese objects from Sichuan (Tamburini et al., 2015). In THM-Py-GC–MS, the homologous series of anisoles and dimethoxybenzenes, which form from phenols and catechols respectively, proved to be equally as characteristic of the three Anacard species as were their underivatized precursors (Heginbotham & Schilling 2011; Petisca et al., 2011; Le Hô et al., 2012).

One significant advantage afforded by TMAH in pyrolysis is that it permits the detection of a number of homologous series formed by aging and oxidation of all three species of Anacard lacquers. For example, Chiavari and Mazzeo (1999) reported an unidentified compound that they detected routinely in Chinese lacquered artifacts; its mass spectrum appears in Fig. 3. This compound, identified in our research as methyl-8-(2,3-dimethoxyphenyl)octanoate, is the \( n = 8 \) member of a series we have termed acid catechols. They are products of oxidation reactions along the unsaturated side chains of substituted catechols, which are analogous in structure to dicarboxylic fatty acids that form by oxidation of unsaturated fatty acids in drying oils. Figure 3 also provides the general structure of methylated acid catechols. Mazzeic acid (\( n = 8 \)) is the dominant member of the

| Table 2 Characteristic ratios for lacquer samples from Figs. 1 and 2 |
|-------------------|---|---|
| Ratios for identification | Red | Black |
| A/P | 0.66 | 0.34 |
| P/S | 1.10 | 1.92 |
| di-C8/di-C9 | 0.32 | 0.53 |
| APAs/monocarboxylic | 0.32 | 0.02 |
| Total fatty acids/glycerol | 91 | 61 |

Figure 3  Structure for methyl-\(n\)-(2,3-dimethoxyphenyl)alkanoate and the mass spectrum for the compound with \(n = 8\).
acid catechol series formed in aged urushi and aged thitsi, whereas arlenic acid \((n = 10)\) is most abundant in aged laccol lacquers.³

A related series of compounds forms in aged thitsi lacquers from oxidation of the unsaturated side chains in alkenyl- benzenes (Fig. 4). In addition, two homologous series of ketones form in aged thitsi by oxidation of the side chains at the alpha-position to the benzene rings (Figs. 5 and 6).

Appendix 2 lists the important markers for Anacard lacquers: dimethoxybenzenes, acid catechols, anisoles, alkyl- and alkenyl-benzenes and their oxidation products, and cashew nut shell liquid (CNSL). Hydrocarbons were omitted from the list because their mass spectra are present in the NIST spectral database, and considering that they define the RI scale \((RI = 100 \times \text{carbon number}; \text{e.g., } RI \text{ for decane is } 1000, \text{dodecane is } 1200, \text{etc.})\), their RI data are already known.

In the literature, extracted ion chromatograms are the most common method of presenting multiple series of Py-GC–MS marker compound classes present in Anacards, yet peaks for unrelated compounds interrupt the regular patterns exhibited by the homologous series and cause confusion. A new option developed in the Getty research utilizes the stacked area graph format in Excel to present peak area data for homologous series of marker compounds. The number of carbon atoms and double bonds is designated on the \(x\)-axis (i.e., \(C_{17}\) is heptadecane, and \(C_{17.1}\) is heptadecene), and peak area is plotted on the \(y\)-axis.⁴ Each compound series is represented by one color in the stacked area graph. We use the term ‘gestalt graph’ to describe this format because the sum of the many compounds represented creates a recognizable visual form that can be used to distinguish the major Anacard types quickly and intuitively.⁵

Figure 7 shows the gestalt graphs for reference samples of aged urushi and aged laccol. In urushi, the homologous series for catechols and hydrocarbons each have a maximum side chain length of \(C_{15}\) with \(C_7\) as the most abundant member of both series, and \(C_8\) (mazzeic acid) is the most abundant acid catechol. In contrast, in aged laccol the chain lengths are \(C_{17}, C_9, \text{and } C_{10}\) (arlenic acid) respectively. Both Anacard lacquers give a series of alkyl benzenes from \(C_3\) to \(C_7\),

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³The authors named the acid catechols after important people in the history of Asian lacquer analysis: Kisaburo Miyama from Imperial University, Tokyo; Ju Kumanotani from the University of Tokyo; Rocco Mazzeo from the University of Bologna; Tetsuo Miyakoshi from Meiji University; Giuseppe Chiavari from the University of Bologna; and Tim Whalen from the GCI. Thitsi oxidation products were named after colleagues who have supported our research: Dr Chu Watanabe; Henk van Keulen; Chris Petersen; and Ulrike Körber. Methyl 13-oxo-13-phenyltridecanoate (tamburinic acid), a thitsi oxidation product, is named after Diego Tamburini, who attended the RADICAL workshop in Paris and made contributions to our study of tannins. Methyl 2-methoxy-6-(8-methoxy-8-oxooctyl)benzoate, the characteristic marker for cashew nut shell liquid, is named after Bettina Ebert, a conservator who studied Vietnamese lacquer paintings in the Witness Collection.

⁴Any problems of incomplete derivatization of catechols by the TMAH reagent in sample preparation may be overcome in data processing by totaling the peak areas for each type of derivative and the underivatized compound into a single value for each member of a homologous series.

⁵The term ‘gestalt’ means something that is made of many parts and yet is somehow more than or different from the combination of its parts. To us, this term seemed apt because users can clearly and easily see the important information for homologous series of lacquer marker compounds when they are represented in Excel stacked area graph format, whereas other graph formats lack such clarity.
which are thought to form by dehydration of alkyl phenols (Le Hô et al., 2012).

Figure 8 shows the gestalt graphs for thitsu lacquer and CNSL lacquer. Phenyl catechols and phenyl phenols are unique markers in thitsu lacquer and alkyl benzenes dominate the gestalt graph. CNSL from Anacardium occidentale is a modern, less expensive substitute for traditional Asian lacquer (Niimura & Miyakoshi, 2003). The gestalt graph for CNSL lacquer is quite unique with its abundance of phenols compared to the other markers. CNSL phenols are meta-substituted, so they elute consistently after the ortho-substituted phenols present in the other Anacard lacquers. Additionally, this lacquer has three marker compounds not present in other Anacards and which do not appear in the gestalt graphs. CNSL has been
discussed in relation to its usage in Vietnamese lacquer paintings in some detail (Ebert & Schilling, 2016).

Gestalt graphs also make it possible to recognize mixtures of Anacards in lacquer samples. Figures 9 and 10 show results for a French commode (c.1750) decorated with Japanese lacquer panels that were made c.1675. It is clear that the relative proportions of phenyl catechols to acid catechols differ between the two samples. The foundation layer is enriched in phenyl catechols that originate from thitsi, whereas the finish layer has a greater proportion of acid catechols, far more than the amount that forms in aged thitsi. Since mazzeic acid is the dominant species, the acid catechols must come from aged urushi; if instead arlenic acid predominated, laccol would have been identified as the source (Heginbotham & Schilling, 2011).

In reviewing marker compound results for samples, the presence of Anacard lacquer is confirmed when catechols, hydrocarbons and alkyl benzenes are all present. Gestalt graphs are consulted to identify the specific type of Anacard lacquer and acid catechols are considered the most distinctive markers.

**Anacard oxidation products**

Although Asian lacquer is an exceptionally durable and stable material, as is evident from its preservation on ancient burial objects, its sensitivity to light is well-documented (Keneghan, 2011). Exposure to light causes profound changes to its surface appearance and sensitivity to solvents (McSharry et al., 2011). To better understand this phenomenon, THM-Py-GC–MS was performed on residues extracted by

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**Figure 7** Gestalt graphs for: (top) aged urushi; and (bottom) aged laccol.
droplets of water applied to the surfaces of Chinese and Japanese export lacquer replica panels that had been exposed to light in an Atlas weatherometer chamber (Webb et al., 2016). Surprisingly, the water extracts were composed almost entirely of isomers of mono-, di-, tri-, and tetra-carboxylated benzene (see Appendix 2), and the lacquer composition affected the final product distribution. These compounds may be largely responsible for the reduction in surface pH as lacquer ages (Webb, 2000). Although the exact mechanism for the formation of these compounds in lacquer is unknown, research on the photochemistry of secondary organic aerosols has shown highly oxidized species form from catechols and substituted phenolics, and that the product distributions are affected by the presence of environmental nitrogen oxides and ozone (Schilling, 2015). Given the relative stability of the catechol ring structures and the absence of phenolic groups in the products, it may be that the side chains are responsible for the formation of carboxylated benzenes in the water extracts of the lacquers (Webb, 2011). Research is needed to investigate the reaction mechanisms for the formation of these compounds and how the residual aged lacquer matrix responds upon their removal during exposure to solvents, which is especially relevant to assessments of conservation treatments involving water or other solvents.

Figure 8 Gestalt graphs for: (top) aged thitsi; and (bottom) aged cashew nut shell liquid.
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Figure 9 Gestalt graph for the ground layer from the Joseph Commode (55.DA.2) in the collection of the JPGM.

Figure 10 Gestalt graph for finish layer on the Joseph Commode (55.DA.2) in the collection of the JPGM.
Proteins
Several proteinaceous materials have been used in Anacard lacquer formulations. Chinese lacquer recipes dating back to the Northern Song dynasty mention the use of whole egg (Chang & Schilling, 2016). Lighter colored grounds on Asian lacquered objects from many countries may contain animal glue (Webb, 2000), whereas traditionally blood has been used in dark ground layers from Chinese and Ryukyuan objects (Körber et al., 2016). At a lacquer craft workshop held at Buffalo State College (Buffalo State College, 2013), Japanese lacquer masters demonstrated the use of tofu as a lightweight filler material that increases the volume of underlying lacquer layers. Markers from all of these materials, sorted by material type in Appendix 3, form by pyrolysis of polypeptides in the presence of TMAH; it should be noted that some are formed by more than one type of protein.

Protein identification in the RAdICAL workbook involves reviewing tables of marker compounds and considering their total peak area in the sample. Other marker compounds that may help confirm the identification are listed in Table 1. Additionally, small amounts of dimethyl sulfide and dimethyl disulfide are formed by the sulfur-containing amino acids in animal glue. Confidence in the identification results is greater when multiple marker compounds for a particular material are present and their total peak area exceeds a few tenths of a percent. Experience has demonstrated that identification of blood and glue in a sample is relatively straightforward because multiple markers are formed by these materials. To date, we have yet to identify tofu or egg in samples from lacquered objects, which may indicate that a broader range of markers is needed. Finally, proteins would not be confirmed in samples if only one or two marker compounds are present at low concentration, because these may originate from naturally occurring enzymes and glycoproteins in the Anacard saps.

Carbohydrates
Carbohydrate marker compounds are listed in Appendix 4. The Chinese lacquer literature mentions rice starch as a common additive in grounds. The history and uses of carbohydrate materials in Japanese lacquer grounds has been explored elsewhere (Heginbotham & Schilling, 2011). Furfural, a generic marker for carbohydrates that appears consistently in pyrograms for starch, is accompanied by a few unverified markers. One such compound was identified in many samples of Chinese and Japanese ground layers supplied to the authors by Nanke Schellmann, who used histochemical stains to study lacquer grounds on objects in the Victoria & Albert Museum (Schellmann, 2012). Ground layers that stained positively for starch with Lugol’s reagent showed an abundant compound in the THM-Py-GC–MS results at 1395 RI units that had a base peak of \( m/z \) 101. The molecular structure of this compound is presently unknown, but the closest NIST library match is 2,3,4-trimethyllevoglucosan. This compound was named Schellmannose to reflect its discovery. A marker named ‘glucoside’ is another generic marker for carbohydrates.

Another category of carbohydrate markers originates from gums and glycoproteins naturally present in Anacard saps. The carbohydrate content of laccol sap is nearly three times higher than that of urushi sap (Kumanotani, 1995). Undetectable without the use of TMAH, these markers have not been reported previously in Py-GC–MS studies of lacquered objects. Two main clusters of carbohydrate peaks appear in THM-Py-GC–MS chromatograms for laccol lacquers. One set that elutes at around 1500 RI units with a base peak of \( m/z \) 129 is likely to relate to pyrolysates that originate from monosaccharides and uronic acids, whereas the second set eluting near 2500 RI units with significant ions at \( m/z \) 101 and \( m/z \) 88 are presumably disaccharide pyrolysates. These compounds are abundant in laccol-containing lacquered objects, often comprising the majority of the total peak area. Conversely, urushi lacquers seldom show measurable amounts of any of these markers. Accordingly, these markers have been designated in Appendix 4 as laccol carbohydrates.

Interpretation and verification of carbohydrate marker compound results in the RAdICAL workbook follow the recommendations described in the section on proteins concerning the presence of multiple markers at levels above a few tenths of a percent.

Resins
Natural resins are an important class of additives in Asian lacquer formulations that affect leveling, gloss, drying rate, aging behavior, and solvent sensitivity. Resins identified in studies of Asian lacquered objects carried out at the Getty include camphor, cedar oil, exudates from Dipterocarpus genus (such as wood oil and dammar), benzoin resin, resins from the Pinacea family and shellac (Heginbotham et al., 2008; Heginbotham & Schilling, 2011; Heginbotham et al., 2016).

Published research on natural resin composition has been an important source of marker compound information in the AMDIS database and the RAdICAL workbook (van Keulen 2014b). Additionally, a number of experts have been especially generous in sharing AMDIS library spectra and interpretation schemes for resins with the authors: Ken Sutherland (shellac); and Chris Petersen (triterpenes). Marker compounds for a number of natural resins identified...
in Asian lacquers are listed in Appendix 5. In the RAdICAL workbook, markers for each resin are tabulated and their total peak areas measured. Marker compounds for resins used exclusively in European lacquers, which are included in the Excel workbook distributed at the RAdICAL workshop, do not appear in Appendix 5 due to the focus of this article.

*Pinaceae* resin was studied extensively by van den Berg and other researchers in the MOLART project (Pastorova et al., 1997); mass spectra for numerous oxidized markers appear in the NIST database. *Pinaceae* resin is confirmed in a sample if, at minimum, the following markers are present: methyl DHA; tetradehydroabietic acid, 7-methoxy-, methyl ester; and 7,15-dimethoxytetradehydroabietic acid, methyl ester. In many Asian lacquer samples, DHA may be present at low concentrations without the other key markers, which suggests the compounds originate from non-resinous materials. In contrast, large proportions of pine resin are customarily added to modern commercial sources of artists’ lacquers in Vietnam (Ebert & Schilling, 2016).

Characterization of shellac has been the focus of research at the Philadelphia Museum of Art by Sutherland, who published mass spectra for numerous marker compounds from different types and sources of shellac (Sutherland & del Rio, 2014). Shellac is confirmed in a sample by the presence of aleuritic acid derivatives, plus aliphatic and cyclic hydroxyacids. Aging or oxidation is indicated by elevated levels of shellolic and laccisHELLOLic acids, as compared to jalaric and laccijalaric acids. Bleached shellac is indicated by a chlorinated lac resin terpene marker with elevated levels of shellolic and laccisHELLOLic acids.

The identification of most of the marker compounds for benzoin resin originated from studies of Egyptian embalming materials (Colombini et al., 2000). These employed a specialized GC–MS procedure involving alkaline hydrolysis and trimethylsilylation to differentiate the two main types of benzoin resin: styrax and benzoe. One limitation of the RAdICAL protocol is that TMAH converts monomethoxy- benzoin marker compounds to dimethoxy- derivatives, which are less characteristic than the original markers for differentiating the two types of benzoin resin. Notwithstanding, the TMAH derivatives in Appendix 5 were identified in a reference standard of Chinese *urushi* mixed with benzoin resin. Gum benzoin is confirmed in lacquer samples if a major amount of 2-propenoic acid, 3-phenyl-, methyl ester is present with three or more other benzoin marker compounds.

**Miscellaneous materials**

Appendix 6 lists marker compounds for a variety of miscellaneous materials that are tabulated in the RAdICAL workbook.

A small number of pigments associated with lacquer are known to give rise to distinctive marker compounds. For example, the pyrolysis of arsenic pigments such as orpiment produces As$_4$O$_6$ and As$_4$ (Chiavari & Mazzeo, 2003; Kamiya et al., 2015); moreover, in the presence of TMAH, the sulfide anion in these pigments forms dimethyl sulfide. Pyrolysis of mercuric sulfide produces elemental mercury vapor, which is evident as a broad baseline rise early in the chromatogram (Chiavari & Mazzeo, 2003; Kamiya et al., 2015). Unfortunately, because elemental mercury elutes as a rise in baseline and not as a well-resolved peak, AMDIS is incapable of identifying it in lacquer analysis results. Its presence can be verified in an extracted ion chromatogram for $m/z$ 202, then noted in the comments section of the RAdICAL workbook. Additionally, the sulfide anion in this pigment also produces dimethyl sulfide and dimethyl disulfide in the presence of TMAH. Three markers for indigo, identified by Poulin (2007) in GC–MS analysis of dyed textiles, were found for green Ryukyuan lacquer that was analyzed using THM-Py–GC–MS (Körber et al., 2016). Finally, bone white and bone black produce trimethyl phosphate, a compound also formed by phospholipids in blood and egg.

Contamination from fingerprints may be detected in lacquer samples by the presence of squalene, cholesterol, and fatty acids. Caffeine may be identified in certain domestic lacquered objects associated with tea, as was the case for a sample from a Taiwanese lacquered tea tray. Presently, there are no known lacquer recipes that mention tea, although the chemical structures of tea catechins are loosely comparable with lacquer components that contain tannins. Finally, Crown 18 is a specific crown ether occasionally detected in Anacard lacquer samples, although a precise mechanism for its formation is currently unknown.

All of the marker compounds tabulated thus far in this article have been verified through extensive research on reference standards and verified in multiple samples from lacquer objects; moreover, the chemical structures for the vast majority have been ascertained and expert knowledge for interpreting the results is available. Accordingly, identification of the corresponding materials in lacquer samples can be carried out with a high degree of certainty using the RAdICAL workbook.

Notwithstanding, there remain a few lacquer materials for which additional research is still needed to validate their corresponding sets of marker compounds. Conversely, there are some markers for which there is insufficient information linking them to a single material. In the RAdICAL workbook, materials and markers in these categories are designated as ‘Provisionally-identified materials’. One important group of substances in this category is tannins, which are complex polyphenolic substances.
that are produced by plants and are often attached to carbohydrate rings (Nakatsuho et al., 2002). Tannins are ubiquitous substances in the plant kingdom and are present in various tissues, including leaves, buds, seeds, roots, stems, and wood. Lacquer-related materials that are known to contain tannins include laccal lacquer (tapped from a Toxicodendron succedanea tree growing in the Los Angeles County Arboretum), fermented persimmon juice (which has been used as a binder in ground layers of Japanese lacquer) and fruit obtained from Bhutanese lacquer trees (da-se) (Kitagawa, 2012). Studies of Chinese and Ryukyuan objects made with laccal revealed the presence of tannin markers at significant levels relative to the other lacquer components. In the RAdICAL workbook, tannin is confirmed in lacquer samples if four or five marker compounds listed in Appendix 6 are present, although with our current set of marker compounds and state of knowledge, the specific plant source for the tannin cannot be identified. Further research on this topic may help differentiate the tannin-containing materials used in lacquers.

Ox gall, mentioned in recipes for black Chinese lacquer (Zhu, 2002), is another provisionally identified material that has been detected in a number of Chinese lacquered objects, including the Chinese lacquered screen mentioned earlier in the section on oils. It was possible to find high probability NIST spectral matches to some of the GC–MS peaks associated with ox gall (Casas-Catalán et al., 2004), whereas lower-quality matches for other peaks correlated to NIST library compounds with similar molecular structures. The gall markers are late-eluting and, with few other compounds within this RI region, they are easy to detect visually in chromatograms. Phosphate and sterol markers often accompany the ox gall markers.

One method for coloring lacquer black is through the addition of a carbon black, in the form of lamp black, soot or bone black. These materials are extremely complex and their formulations depend on the source material, heating conditions and method of collection (Watson & Valberg, 2001; Achten et al., 2015). A small number of polycyclic aromatic compounds have been observed in black lacquers that are absent in transparent lacquers, and these have been assigned to soot in the RAdICAL workbook. Often, these markers are accompanied by small amounts of methyl DHA and other Pinaceae resin markers. If instead trimethyl phosphate is present, this is indicative of bone black.

Gamboge is another material for which the set of marker compounds in Appendix 6 requires confirmation. The gamboge markers in Appendix 6 originate from late-eluting peaks in the chromatogram for a yellow-tinted Japanese lacquered object for which compounds with similar, but not identical, mass spectra were identified in reference samples of Asian gamboge mixed into Anacard lacquer (Heginbotham & Schilling, 2011). Further research into the identification of this material is needed.

Conclusions

The combination of THM-Py-GC–MS with the RAdICAL expert system for data evaluation represents a powerful tool for characterizing organic materials in Asian lacquers. Compared to Py-GC–MS, pyrolysis in the presence of TMAH yields a much broader range of characteristic marker compounds. No other analytical technique is capable of identifying Anacard saps and the full range of known additives in Asian lacquers, even in objects buried for more than 2000 years. Improvements in pyrolyzer technology have reduced the required sample size, making it possible to analyze powder samples taken from individual lacquer layers as small as 20 μm in thickness.

The RAdICAL expert system overcomes many difficulties encountered in evaluating Py-GC–MS data. AMDIS is, without question, the best way of processing Py-GC–MS data files to identify compounds in lacquer samples. The program is fast, precise, accurate and systematic, and the results are repeatable. Based on our experience of teaching AMDIS in RAdICAL workshops, even newcomers to Py-GC–MS are capable of using the program to identify hundreds of marker compounds routinely and accurately in unknown lacquer samples. The only limit to the applicability of AMDIS to material characterization is the breadth of the target compound library. AMDIS components not matched to a RAdICAL library spectrum are clearly marked in the program window, allowing users the option of searching the full NIST database to identify the component, or adding the mass spectrum for the unknown component to a library. Substitution of a library entry number into the ‘Ref. Ion’ field for each target compound in the AMDIS library has opened the possibility of systematic processing of the AMDIS report by Excel. The downside of this substitution is the loss of automated signal-to-noise calculations for the target compounds. It would be beneficial if NIST would add a library entry number field to the next revision of AMDIS. The customized RAdICAL Excel workbook accepts the AMDIS report that lists marker compounds identified in a sample and reorganizes them by class of artists’ materials, making it possible to perform calculations and display sorted information for each material in graphs and tables. Expert knowledge relating materials to their associated marker compounds, obtained from publications and personal communications and which has been embedded into the Excel worksheets, permits researchers to make informed decisions about the presence or absence of materials in their lacquer samples.
Identification of additives in Asian lacquers continues to be an important research topic. As demonstrated by the work of Chang and Schilling (2016), much relevant information on lacquer formulations and additives has been published in languages other than English. Therefore, a systematic review of lacquer literature from Japan, Korea, Vietnam, Burma, and Thailand, and translation into English would make this vast body of knowledge accessible to researchers outside these countries. Such work would expand the known range of lacquer materials and formulations that should be studied, and provide complementary information to existing technical studies of objects from these countries. From the analytical perspective, it should be recognized that pyrolysis pathways leading to marker compound formation are affected by the sample matrix, meaning that marker compounds formed by a material may differ from those produced by the same material mixed with raw lacquer. Thus, the identification of lacquer materials will improve through study of lacquer replicas formulated using a broad range of additives mixed into lacquer.

The standardized data formats of AMDIS and Excel facilitate the sharing of results with other researchers using the Radical protocol, thereby encouraging cross-comparison of interpreted results, collaboration and expansion of the lacquer community. AMDIS was designed to open data files from most GC–MS instrument manufacturers, and has the option of opening the generic format net cdf files from any instrument so that, theoretically, anyone analyzing Asian lacquer with PyGC–MS may benefit from the Radical protocol. We encourage researchers of Asian lacquer to share their marker compounds and schemes for interpreting the results with us, so their expert knowledge can be integrated into the expert system and improve its current capabilities, and shared with Radical alumni and others in the lacquer community. As marker compounds for new materials are added to the library, and supplemental markers are added to improve the identification of materials already in the database, the lacquer community will be presented with opportunities for the periodic re-evaluation of existing test data in order to search for the suite of new materials and markers in their lacquered objects. One hope is that this process will lead to a shared database of raw PyGC–MS data files and Radical reports for objects that are accessible to all lacquer researchers. Finally, Radical alumni familiar with Excel have developed other presentation formats better suited to represent their test results, which highlights the flexibility of the system.

This article provides supplementary information for readers to better understand the analytical results presented in other articles in this issue that were obtained from the Radical protocol. It is hoped that readers will appreciate the breadth and depth of information that can be obtained by the protocol and the value of presenting test results for lacquered objects in standardized formats that facilitate comparisons.

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gardenia extract; and Samnang Huot, National Museum of Cambodia, for wood oil and Cambodian lacquer.

Suppliers
Raw laccol from Phú Thọ province in northern Vietnam, son diệu lacquer from the south of Vietnam, Cambodian lacquer: Asiatra Foundation.

Seed lac: H. Behlen (www.shellac.net/behlen-wood-finishing.html).

Gum benzoin, gamboge: Kremer Pigmente (http://kremer-pigmente.de/en).

Japanese urushi, Chinese urushi, Taiwanese laccol, tung oil: Long Nan Museum of National Lacquerware, No. 211-1 Beiping St., Puli Township, Nantou, Taiwan.

Sesame oil: Sigma-Aldrich (www.sigmaaldrich.com/united-states.html).

Tung oil, perilla oil: Tokyo Hands Store, 1-9-1 Marunouchi, Chiyoda, Tokyo 100-6701, Japan.

Chinese raw urushi, Japanese roiro, fermented persimmon juice: Watanabe-Shoten, 6-5-8 Ueno, Taito-ku, Tokyo 110-0005 Japan.

Purple Shiso seeds (Perilla frutescens nankinensis): Whatcom Seed Company, 4419 Hyacinth St, Eugene, OR 97404, USA.

Ox gall: Winsor & Newton (www.winsornewton.com/na/).

References
Achten, C., Beer, F.T., Stader, C. & Brinkhaus, S.G. 2015. Wood-Specific Polycyclic Aromatic Hydrocarbon (PAH) Patterns in Soot Using Gas Chromatography-Atmospheric Pressure Laser Ionization-Mass Spectrometry. Environmental Forensics, 16(1): 42–50.

Buffalo State College. 2013. Asian Lacquer Symposium [accessed 17 June 2016]. Available at: <http://artconservation.buffalostate.edu/news/asian-lacquer-symposium-gathers-international-experts>.

Casas-Catàlan, M.J., Domènech-Carbó, M.T., Mateo-Castro, R., Gimeno-Adelantado, J.V. & Bosch-Reig, F. 2004. Characterization of Bile Acids and Fatty Acids From Ox Bile in Oil Paintings by Gas Chromatography–mass Spectrometry. Journal of Chromatography A, 1025: 269–76.

Chang, J. & Schilling, M.R. 2016. Reconstructing Lacquer Technology Through Chinese Classical Texts. Studies in Conservation. doi:10.1080/00393630.2016.1227115

Chen, Y., Zlatkis, A., Middleditch, B.S., Cowles, J. & Scheld, W. 1987. Lipids of Contemporary Stillingia Oil. Chromatographia, 23(4): 240–2.

Chiavari, G. & Mazzeo, R. 1999. Characterization of Paint Layers in Chinese Archaeological Relics by Pyrolysis-GC-MS. Chromatographia, 49(5–6): 268–72.

Chiavari, G. & Mazzeo, R. 2003. Analytical Pyrolysis as Diagnostic Tool in the Investigation of Works of Art. Chromatographia, 58 (9–10): 543–54.

Colombini, M.P., Modugno, F., Silvano, F. & Onor, M. 2000. Characterization of the Balm of an Egyptian Mummy from the Seventh Century B.C. Studies in Conservation, 45: 19–29.

Ebert, B. & Schilling, M.R. 2016. A Technical Analysis of Paint Media Used in Twentieth-century Vietnamese Lacquer Paintings. Studies in Conservation. doi:10.1080/00393630.2016.1227051

Evershed, R.P. 2007. Exploiting Molecular and Isotopic Signals at the Mesolithic-Neolithic Transition. Proceedings of the British Academy, 144: 141–64.

Frate, J.C., Ribeiro, M.I., Graca, J. & Rodrigues, J. 2009. Applying Pyrolysis-Gas Chromatography/Mass Spectrometry to the Identification of Oriental Lacquers: Study of Two Lacquered Shields. Analytical and Bioanalytical Chemistry, 395(7): 2167–74.

Getty Conservation Institute. 2016. Recent Advances in Characterizing Asian Lacquer [accessed 1 May 2016]. Available at: <www.getty.edu/conservation/our_projects/education/radical/index.html>.

Heginbotham, A., Chang, J., Khandjian, H. & Schilling, M.R. 2016. Some Observations on the Composition of Chinese Lacquer. Studies in Conservation. doi:10.1080/00393630.2016.1269079

Heginbotham, A., Khandjian, H., Rivenc, R. & Schilling, M. 2008. A Procedure for the Efficient and Simultaneous Analysis of Asian and European Lacquers in Furniture of Mixed Origin. In: J. Bridgland, ed. ICOM Committee for Conservation 15th Triennial Meeting New Delhi Preprints. New Delhi: Allied Publishers, vol. II, pp. 608–16.

Heginbotham, A. & Schilling, M. 2011. New Evidence for the Use of Southeast Asian Raw Materials in Seventeenth-Century Japanese Export Lacquer. In: S. Rivers, R. Faulkner & B. Pretzel, eds. East Asian Lacquer: Material Culture, Science and Conservation. London: Archetype, pp. 92–106.

Honda, T., Lu, R., Kitano, N., Kamiya, Y. & Miyakoshi, T. 2010. Applied Analysis and Identification of Ancient Lacquer Based on Pyrolysis-Gas Chromatography/Mass Spectrometry. Journal of Applied Polymer Science, 118: 987–901.

Honda, T., Lu, R., Yamabuki, M., Ando, D., Miyaizato, M., Yoshida, K. & Miyakoshi, T. 2015. Investigation of Ryukyu Lacquerwares by Pyrolysis-Gas Chromatography/Mass Spectrometry. Journal of Applied and Analytical Pyrolysis, 113: 41–5.

Jameson, G.S. & McKinney, R.S. 1938. Stillingga Oil. Oil & Soap, 15(11): 295–6.

Kamiya, Y., Honda, T., Ohbuchi, A. & Miyakoshi, T. 2015. Simultaneous Organic and Inorganic Analysis of Colored Oriental Lacquerware by Pyrolysis-Gas Chromatography/mass Spectrometry. International Journal of Polymer Science, Article 725467. Available at: <http://dx.doi.org/10.1155/2015/725467>.

Keneghan, B. 2011. Developing a Methodology for the Artificial Ageing of urushi and a Preliminary Examination of Urushi-Based Conservation Options. In: S. Rivers, R. Faulkner & B. Pretzel, eds. East Asian Lacquer: Material Culture, Science and Conservation. London: Archetype, pp. 51–9.

Khanjian, H., Schilling, M.R., Lee, L. & Heginbotham, A. 2011. Report on the Analysis of Chinese Lacquered Objects from the Huan Provincial Museum. Getty Conservation Institute internal report.

Kitagawa, M. 2012. Internal Report on Bhutanese Lacquered Object Studied in the RAIDICAL Workshop that was Held at the Getty Conservation Institute in October 2012.

Körber, U., Schilling, M.R., Barrocas Dias, C. & Dias, L. 2016. Simplified Chinese Lacquer Techniques and Namban Style Decoration on Luso-Asian Objects from the Late 16th or Early 17th Century. Studies in Conservation. doi:10.1080/00393630.2016.1227052

Kumanotani, J. 1995. Urushi (oriental lacquer) — a Natural Aesthetic Durable and Future-Promising Coating. Progress in Organic Coatings, 26: 163–95.

Le Hô, A.S., Regert, M., Marascot, O., Duhamel, C. & Langlois, J. 2015. Simplified Chinese Lacquer Techniques and a Preliminary Examination of Urushi-Based Conservation Options. In: S. Rivers, R. Faulkner & B. Pretzel, eds. East Asian Lacquer: Material Culture, Science and Conservation. London: Archetype, pp. 92–106.

McSharry, C., Faulkner, R., Rivers, S., Shaffer, M.S.P. & Welton, T. 2011. Solvent Effects on East Asian Lacquer. In: S. Rivers, R. Faulkner & B. Pretzel, eds. East Asian Lacquer: Material Culture, Science and Conservation. London: Archetype, pp. 60–74.

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Mills, J.S. 1966. The Gas Chromatographic Examination of Paint Media. Part I: Fatty Acid Composition and identification of dried oil films. Studies in Conservation, 11: 92–107.

Nakatsuho, F., Enokita, K., Murakami, K., Yonemori, K., Sugiura, A., Utsunomiya, N. & Subhadra Bhasha, S. 2002. Chemical Structures of the Condensed Tannins in the Fruits of Diospyros Species. Journal of Wood Science, 48(5): 414–8.

Niimura, N. & Miyakoshi, T. 2000. Identification of Oriental Lacquer Films using Pyrolysis-Gas Chromatography/Mass Spectrometry. In: M. Kühlethaler, ed. Japanische und europäische Lackarbeiten: Rezeption, Adaption, Restaurierung / Japanese and European Lacquervare: Adoption, Adaptation, Conservation. Munich: Bayerischen Landesamtes für Denkmalpflege, pp. 123–34.

Niimura, N. & Miyakoshi, T. 2003. Characterization of Natural Resin Films and Identification of Ancient Coating. Journal of the Mass Spectrometry Society of Japan, 51(4): 439–57.

Niimura, N., Miyakoshi, T., Onodera, J. & Higuchi, T. 1999. Identification of Ancient Lacquer Film Using Two-Stage Pyrolysis-Gas Chromatography/Mass Spectrometry. Archaeometry, 41(1): 137–49.

NIST. 2016. [accessed 1 May 2016]. AMDIS. Available at: <http://chemdata.nist.gov/dokuwiki/doku.php?id=chemdata:amdis:>

Pastorova, I., van der Berg, K.J., Boon, J.J. & Verhoeven, J.W. 1997. Analysis of Oxidised Diterpenoid Acids Using Thermally Assisted Methylation with TMAH. Journal of Analytical and Applied Pyrolysis, 43(1): 41–57.

Petitsa, M.J., Frade, J.C., Cavaco, M., Ribeiro, I., Candeias, A., Guarro, J. & Ribeiro, J. 2011. Chinese Export Lacquere: Characterisation of a Group of Canton Lacquer Pieces from the 18th and 19th Centuries. In: J. Bridgland, ed. ICOM Committee for Conservation 16th Triennial Meeting Lisbon Preprints. Almada: Critério, paper 2106, pp. 1–8.

Pithard, V., Stanek, S., Griesser, M., Jordan, C., Muklin-Kniefacz, S. & Miklin, R. 2016. The Technical Investigation of an Eighteenth-Century Chinese Imperial Carved Lacquer Screen and its Role in Developing an Appropriate Conservation Treatment. Studies in Conservation (this issue).

Poulin, J. 2007. Identification of Indigo and its Degradation Products on a Silk Textile Fragment Using Gas Chromatography-Mass Spectrometry. Journal of the Canadian Association for Conservation, 32: 48–56.

Schellmann, N. 2012. Consolidation of Stressed and Lifting Decorative Coatings on Wood — the Effect of Consolidant choice on the Structural Integrity of Multilayered East Asian Lacquer Coatings with Gesso-type Foundation Layers. Doctoral thesis. Dresden: Academy of Fine Arts Dresden.

Schilling, K.A. 2015. Secondary Organic Aerosol Composition Studies Using Mass Spectrometry. Doctoral dissertation. California Institute of Technology [accessed 1 May 2016]. Available at: <http://resolver.caltech.edu/CaltechTHESIS:05222015-145550415>

Stein, S.E. 1999. An Integrated Method for Spectrum Extraction and Compound Identification from GC-MS data. Journal of the American Society of Mass Spectrometry, 10: 770–81.

Sutherland, K. & del Rio, J.C. 2014. Characterisation and Discrimination of Various Types of Lac Resin Using Gas Chromatography Mass Spectrometry Techniques with Quaternary Ammonium Reagents. Journal of Chromatography A, 1338: 149–63.

Tamburini, D., Bonaduce, I. & Colombini, M.P. 2015. Characterization and Identification of Urushi Using in situ Pyrolysis/Silylation-Gas Chromatography-Mass Spectrometry. Journal of Analytical and Applied Pyrolysis, 111: 33–40.

van Keulen, H. 2014a. Slow-Drying Oil Additives in Modern Oil Paints and Their Application in Conservation Treatments. An Analytical Study in Technical Historical Perspective. In: J. Bridgland, ed. ICOM Committee for Conservation 17th Triennial Meeting Melbourne Preprints. Paris: International Council of Museums, paper 1316, pp. 1–8.

van Keulen, H. 2014b. The Analysis and Identification of Transparent Finishes Using Thermally Assisted Hydrolysis and Methylation Pyrolysis-Gas Chromatography-Mass Spectrometry. In: M.V. Dias, ed. Twelfth International Symposium on Wood and Furniture Conservation. Amsterdam: Stichting Ebenist, pp. 334–41.

Watson, A.Y. & Valberg, P.A. 2001. Carbon Black and Soot: Two Different Substances. Journal of the American Industrial Hygiene Association, 62(2): 218–28.

Webb, M. 2000. Lacquer: Technology and Conservation. Oxford: Butterworth-Heinemann.

Webb, M. 2011. The Autofluorescence of Asian Lacquer. In: S. Rivers, R. Faulkner & B. Pretzel, eds. East Asian Lacquer: Material Culture, Science and Conservation. London: Archetype, pp. 148–58.

Webb, M., Schilling, M.R. & Chang, J. 2016. The Reproduction of Realistic Samples of Chinese Export Lacquer for Research. Studies in Conservation. doi:10.1080/00393630.2016.1227116

Yuasa, K., Honda, T., Lu, R., Hachiya, T. & Miyakoshi, T. 2015. Analysis of Japanese Ancient Lacquerwares Excavated from Jōmon Period Ruins. Journal of Analytical and Applied Pyrolysis, 113: 73–7.

Zhu, F. 2002. Yu gu zhai qin pu. Shanghai: Shanghai gu ji chu ban she.
### Appendix 1. THM-Py-GC–MS marker compounds for oils and lipids

| Target compound name | RI | Formula | MW | Ion 1 | Ion 2 | Ion 3 | Ion 4 | Ion 5 |
|----------------------|----|---------|----|-------|-------|-------|-------|-------|
| **Monocarboxylic fatty acid methyl esters** |    |         |    |       |       |       |       |       |
| Butanoic acid, methyl ester | 720 | C<sub>4</sub>H<sub>6</sub>O<sub>2</sub> | 102 | 43 | 74 | 71 | 59 | 87 |
| Octanoic acid, methyl ester | 1142 | C<sub>8</sub>H<sub>14</sub>O<sub>2</sub> | 130 | 74 | 87 | 43 | 99 | 59 |
| Hexanoic acid, methyl ester | 962 | C<sub>6</sub>H<sub>12</sub>O<sub>2</sub> | 128 | 74 | 87 | 43 | 99 | 59 |
| 5-Hexenoic acid, methyl ester | 938 | C<sub>6</sub>H<sub>12</sub>O<sub>2</sub> | 128 | 74 | 87 | 43 | 99 | 59 |
| Pentanoic acid, methyl ester | 830 | C<sub>9</sub>H<sub>14</sub>O<sub>2</sub> | 130 | 74 | 87 | 43 | 99 | 59 |
| 7-Octenoic acid, methyl ester | 1135 | C<sub>9</sub>H<sub>18</sub>O<sub>2</sub> | 158 | 74 | 87 | 127 | 115 | 158 |
| 8-Nonenonic acid, methyl ester | 1218.1 | C<sub>10</sub>H<sub>20</sub>O<sub>2</sub> | 170 | 74 | 87 | 129 | 141 | 172 |
| 8-Nonanoic acid, methyl ester | 1226.5 | C<sub>10</sub>H<sub>20</sub>O<sub>2</sub> | 172 | 74 | 87 | 129 | 141 | 172 |
| 6-Heptenoic acid, methyl ester | 1046 | C<sub>8</sub>H<sub>14</sub>O<sub>2</sub> | 142 | 74 | 41 | 55 | 68 | 110 |
| Heptanoic acid, methyl ester | 1054 | C<sub>9</sub>H<sub>16</sub>O<sub>2</sub> | 156 | 74 | 55 | 43 | 40 | 125 |
| 9-Octadecenoic acid (Z)-, methyl ester | 2103 | C<sub>18</sub>H<sub>36</sub>O<sub>2</sub> | 296 | 74 | 125 | 115 | 155 | 186 |
| Octadecanoic acid, methyl ester | 2192 | C<sub>19</sub>H<sub>38</sub>O<sub>2</sub> | 298 | 74 | 129 | 143 | 158 | 214 |
| 8,11-Octadecadienoic acid, methyl ester | 2265 | C<sub>19</sub>H<sub>38</sub>O<sub>2</sub> | 299 | 74 | 129 | 143 | 158 | 214 |
| Nonadecanoic acid, methyl ester | 2360 | C<sub>20</sub>H<sub>40</sub>O<sub>2</sub> | 312 | 74 | 129 | 143 | 158 | 214 |
| Eicosanoic acid, methyl ester | 2455 | C<sub>21</sub>H<sub>42</sub>O<sub>2</sub> | 326 | 74 | 129 | 143 | 158 | 214 |
| Heneicosanoic acid, methyl ester | 2550 | C<sub>22</sub>H<sub>44</sub>O<sub>2</sub> | 340 | 74 | 129 | 143 | 158 | 214 |
| 9-Octadecenoic acid (Z)-, methyl ester | 2645 | C<sub>23</sub>H<sub>44</sub>O<sub>2</sub> | 352 | 74 | 129 | 143 | 158 | 214 |
| Octadecanoic acid, methyl ester | 2740 | C<sub>24</sub>H<sub>46</sub>O<sub>2</sub> | 366 | 74 | 129 | 143 | 158 | 214 |
| Nonadecanoic acid, methyl ester | 2835 | C<sub>25</sub>H<sub>48</sub>O<sub>2</sub> | 380 | 74 | 129 | 143 | 158 | 214 |
| Dodecanedioic acid, methyl ester | 2930 | C<sub>26</sub>H<sub>50</sub>O<sub>2</sub> | 394 | 74 | 129 | 143 | 158 | 214 |
| Tetracosenoic acid, methyl ester | 3025 | C<sub>27</sub>H<sub>52</sub>O<sub>2</sub> | 408 | 74 | 129 | 143 | 158 | 214 |
| 13-Octadecosenoic acid, methyl ester | 3120 | C<sub>28</sub>H<sub>54</sub>O<sub>2</sub> | 422 | 74 | 129 | 143 | 158 | 214 |
| Polyunsaturated fatty acid methyl esters | 3215 | C<sub>29</sub>H<sub>56</sub>O<sub>2</sub> | 436 | 74 | 129 | 143 | 158 | 214 |
| 13-Docosenoic acid, methyl ester | 3310 | C<sub>30</sub>H<sub>60</sub>O<sub>2</sub> | 450 | 74 | 129 | 143 | 158 | 214 |
| 24-Docosenoic acid, methyl ester | 3405 | C<sub>31</sub>H<sub>62</sub>O<sub>2</sub> | 464 | 74 | 129 | 143 | 158 | 214 |
| Tetraicosanoic acid, methyl ester | 3500 | C<sub>32</sub>H<sub>64</sub>O<sub>2</sub> | 480 | 74 | 129 | 143 | 158 | 214 |
| Undecanedioic acid, methyl ester | 3605 | C<sub>33</sub>H<sub>66</sub>O<sub>2</sub> | 494 | 74 | 129 | 143 | 158 | 214 |
|2-Propanol, 1,3-dimethoxy- | 890 | C<sub>4</sub>H<sub>8</sub>O<sub>3</sub> | 120 | 45 | 75 | 43 | 71 | 102 |
| Propane, 1,2,3-trimethoxy- | 916.4 | C<sub>6</sub>H<sub>14</sub>O<sub>3</sub> | 134 | 59 | 89 | 45 | 58 | 102 |
|2,3-Dimethoxypropan-1-ol | 930 | C<sub>4</sub>H<sub>8</sub>O<sub>3</sub> | 106 | 45 | 58 | 75 | 89 | 59 |
### Appendix 2. THM-Py-GC–MS marker compounds for Anacardiaceae tree saps

| Target compound name                                      | Rt  | Formula      | MW  | Ion 1 | Ion 2 | Ion 3 | Ion 4 | Ion 5 |
|-----------------------------------------------------------|-----|--------------|-----|-------|-------|-------|-------|-------|
| **Substituted dimethoxybenzenes (from catechols)**        |     |              |     |       |       |       |       |       |
| 1,2-Dimethoxy-3-ethylbenzene                              | 1259| C₁₀H₁₂O₂     | 166 | 136   | 118   | 120   | 162   |
| 1,2-Dimethoxy-3-propylbenzene                             | 1338| C₁₁H₁₄O₂     | 180 | 136   | 151   | 91    | 192   |
| 1,2-Dimethoxy-3-butylbenzene                              | 1401.6| C₁₂H₁₄O₂   | 192 | 136   | 151   | 91    | 131   |
| 1,2-Dimethoxy-3-butybenzene                               | 1430| C₁₂H₁₄O₂     | 194 | 136   | 151   | 91    | 152   |
| 1,2-Dimethoxy-3-hexylbenzene                              | 1615| C₁₄H₂₀O₂     | 220 | 136   | 151   | 220   | 91    |
| 1,2-Dimethoxy-3-hexenylbenzene                            | 1622| C₁₄H₂₀O₂     | 222 | 136   | 222   | 91    | 77    |
| 1,2-Dimethoxy-3-heptylbenzene                             | 1715| C₁₅H₂₂O₂     | 234 | 136   | 91    | 152   | 234   |
| 1,2-Dimethoxy-3-heptylbenzene                             | 1723| C₁₅H₂₂O₂     | 236 | 136   | 236   | 152   | 91    |
| 1,2-Dimethoxy-3-octylbenzene                              | 1815| C₁₆H₂₄O₂     | 248 | 136   | 248   | 152   | 91    |
| 1,2-Dimethoxy-3-octylbenzene                              | 1823| C₁₆H₂₄O₂     | 250 | 136   | 152   | 91    |
| 1,2-Dimethoxy-3-nonylbenzene                              | 1921| C₁₇H₂₆O₂     | 264 | 136   | 264   | 152   |
| 1,2-Dimethoxy-3-decylnbenzene                             | 2140| C₁₈H₃₀O₂     | 278 | 136   | 278   | 151   |
| 1,2-Dimethoxy-3-pentadec-8-ethylbenzene                   | 2533| C₂₁H₃₆O₂     | 346 | 136   | 346   | 152   |
| 1,2-Dimethoxy-3-pentadecylbenzene                         | 2552| C₂₁H₃₆O₂     | 348 | 136   | 348   | 152   |
| 1,2-Dimethoxy-3-heptadec-10-ethylbenzene                  | 2707| C₂₅H₄₂O₂     | 374 | 136   | 374   | 152   |
| 1,2-Dimethoxy-3-heptadecylbenzene                         | 2755| C₂₅H₄₂O₂     | 376 | 151   | 376   | 152   |
| 1,2-Dimethoxy-10-phenyldecylbenzene                       | 2791| C₂₄H₃₆O₂     | 354 | 136   | 354   | 152   |
| 1,2-Dimethoxy-12-phenyldodecylbenzene                     | 3007| C₂₆H₄₀O₂     | 382 | 136   | 382   | 152   |
| **Acid catechols (catechol oxidation products)**           |     |              |     |       |       |       |       |       |
| Methyl 6-(2,3-dimethoxyphenyl)hexanoate (miyamic acid)     | 1954| C₁₅H₂₂O₄     | 266 | 136   | 266   | 91    | 121   |
| Methyl 7-(2,3-dimethoxyphenyl)heptanoate (kumanotinic acid)| 2056| C₁₆H₂₄O₄     | 280 | 136   | 280   | 151   |
| Methyl 8-(2,3-dimethoxyphenyl)octanoate (mazzeic acid)     | 2158| C₁₇H₂₆O₄     | 294 | 136   | 294   | 151   |
| Methyl 9-(2,3-dimethoxyphenyl)nonanoate (miyakoshic acid)  | 2261| C₁₈H₂₈O₄     | 308 | 136   | 308   | 151   |
| Methyl 10-(2,3-dimethoxyphenyl)dectanoate (arlenic acid)   | 2364| C₁₉H₃₂O₄     | 322 | 136   | 322   | 152   |
| Methyl 11-(2,3-dimethoxyphenyl)dodecanoate (whalenic acid)| 2468| C₂₀H₃₄O₄     | 336 | 136   | 336   | 151   |
| Methyl 12-(2,3-dimethoxyphenyl)dodecanoate (chiavaric acid)| 2567| C₂₁H₃₆O₄     | 350 | 136   | 350   | 152   |
| **Anisoles (from phenols)**                                |     |              |     |       |       |       |       |       |
| 2-Hexylanisole                                             | 1495.9| C₁₃H₂₀O     | 192 | 122   | 122   | 93    |
| 2-Heptylanisole                                            | 1595| C₁₄H₂₂O     | 206 | 122   | 121   | 206   |
| 2- Octylanisole                                            | 1698.7| C₁₅H₂₄O     | 220 | 122   | 186   | 220   |
| 2-Pentadecylanisole                                        | 2440| C₂₂H₃₄O     | 316 | 122   | 121   | 316   |
| 2-Pentadecylanisole                                        | 2424.7| C₂₂H₃₄O     | 318 | 122   | 121   |
| 2-Heptadecylanisole                                        | 2614.3| C₂₄H₄₀O     | 344 | 215   | 344   |
| 12-Phenyldecylanisole                                      | 2901| C₂₅H₃₆O     | 352 | 122   | 121   |
| **Alkyl- and alkenyl-benzenes**                            |     |              |     |       |       |       |       |       |
| Benzene, 1-propenyl-                                       | 983 | C₉H₁₀       | 118 | 117   | 118   | 91    |
| Benzene, propyl-                                           | 992 | C₁₀H₁₂      | 120 | 91    | 120   | 92    |
| Benzene, 3-butyl-                                          | 1079| C₁₀H₁₄      | 132 | 91    | 132   | 65    |
| Benzene, butyl-                                            | 1091| C₁₁H₁₄      | 134 | 91    | 92    | 134   |
| Benzene, 4-pentenyl-                                       | 1163| C₁₁H₁₄      | 146 | 91    | 92    |
| Benzene, pentyl-                                           | 1177| C₁₁H₁₆      | 148 | 91    | 92    |
| Benzene, 4-hexenyl-                                        | 1270| C₁₂H₁₆      | 160 | 91    | 92    |
| Benzene, hexyl-                                            | 1277| C₁₂H₁₈      | 162 | 91    | 92    |
| Benzene, 5-heptenyl-                                       | 1369| C₁₃H₁₈      | 174 | 91    | 92    |
| Benzene, heptyl-                                           | 1377| C₁₃H₂₀      | 176 | 91    | 92    |
| Octenyl benzene                                            | 1474| C₁₃H₂₀      | 188 | 91    | 104   |
| Benzene, octyl-                                            | 1482| C₁₄H₂₂      | 190 | 91    | 92    |
| Nonenyl benzene                                            | 1577| C₁₅H₂₂      | 202 | 91    | 104   |
| Nonyl benzene                                              | 1584| C₁₅H₂₄      | 204 | 91    | 92    |
| Decenyl benzene                                            | 1684| C₁₆H₂₄      | 216 | 91    | 104   | 92 |

Continued
### Appendix 2. Continued

| Target compound name | RI | Formula | MW | Ion 1 | Ion 2 | Ion 3 | Ion 4 | Ion 5 |
|----------------------|----|---------|----|-------|-------|-------|-------|-------|
| Benzene, decyl-      | 1690 | C₁₆H₃₆ | 218 | 92    | 91    | 218   | 105   | 133   |
| Undecenyl benzene    | 1786 | C₁₇H₃₈ | 230 | 91    | 104   | 117   | 230   | 131   |
| Benzene, undecyl-    | 1793 | C₁₇H₃₈ | 232 | 92    | 91    | 232   | 105   | 133   |
| Dodecenyl benzene    | 1894 | C₁₈H₃₈ | 244 | 91    | 104   | 92    | 117   | 244   |
| Benzene, dodecyl-    | 1900 | C₁₈H₃ₐ | 246 | 92    | 91    | 246   | 105   | 133   |
| Tridecyl benzene     | 2003 | C₁₉H₃₂ | 260 | 92    | 91    | 260   | 57    | 133   |

**Oxidation products of alkenyl-benzenes**

| Target compound name | RI | Formula | MW | Ion 1 | Ion 2 | Ion 3 | Ion 4 | Ion 5 |
|----------------------|----|---------|----|-------|-------|-------|-------|-------|
| Methyl 9-phenyl-nonanoate (poulinic acid) | 1925 | C₁₆H₂₄O₂ | 248 | 91    | 92    | 104   | 216   | 248   |
| Methyl 10-phenyl-decanoate (körberic acid) | 2029 | C₁₇H₂₆O₂ | 262 | 91    | 92    | 104   | 230   | 262   |
| Methyl 11-phenyl-undecanoate (watanabic acid) | 2136 | C₁₈H₃₈O₂ | 276 | 91    | 92    | 104   | 244   | 276   |
| Methyl 12-phenyl-dodecanoate (szelewskic acid) | 2241 | C₁₉H₃₂O₂ | 290 | 91    | 92    | 104   | 258   | 290   |
| Methyl 13-phenyl-tridecanoate (keulenic acid) | 2347 | C₂₀H₃₄O₂ | 304 | 91    | 92    | 104   | 265   | 304   |

**Ketone oxidation products of thitsi**

| Target compound name | RI | Formula | MW | Ion 1 | Ion 2 | Ion 3 | Ion 4 | Ion 5 |
|----------------------|----|---------|----|-------|-------|-------|-------|-------|
| Methyl 9-oxo-9-phenylnonanoate | 2141 | C₁₆H₂₄O₃ | 262 | 120   | 105   | 77    | 133   | 262   |
| Methyl 10-oxo-10-phenyldecanoate | 2250 | C₁₇H₂₆O₃ | 276 | 120   | 105   | 77    | 133   | 276   |
| Methyl 11-oxo-11-phenylundecanoate | 2355 | C₁₈H₃₈O₃ | 290 | 120   | 105   | 77    | 133   | 290   |
| Methyl 12-oxo-12-phenyldodecanoate | 2462 | C₁₉H₃₆O₃ | 304 | 120   | 105   | 77    | 133   | 304   |
| Methyl 13-oxo-13-phenyltridecanoate (tamburinic acid) | 2569 | C₂₀H₃₄O₃ | 318 | 120   | 105   | 77    | 133   | 318   |

**Cashew nut shell liquid markers**

| Target compound name | RI | Formula | MW | Ion 1 | Ion 2 | Ion 3 | Ion 4 | Ion 5 |
|----------------------|----|---------|----|-------|-------|-------|-------|-------|
| Methyl 8-(3-methoxyphenoxy)octanoate | 2049 | C₁₈H₂₄O₃ | 264 | 122   | 121   | 264   | 135   | 91    |
| Methyl 2-methoxy-6-(8-methoxy-8-oxooctyl)benzoate (ebertic acid) | 2329.1 | C₁₈H₂₆O₅ | 322 | 161   | 291   | 290   | 272   | 175   |

**Anacard oxidation products**

| Target compound name | RI | Formula | MW | Ion 1 | Ion 2 | Ion 3 | Ion 4 | Ion 5 |
|----------------------|----|---------|----|-------|-------|-------|-------|-------|
| Benzoic acid, methyl ester | 1126 | C₆H₅O₂ | 136 | 105   | 77    | 136   | 51    | 106   |
| 1,4-Benzenedicarboxylic acid, dimethyl ester | 1514 | C₁₀H₁₀O₄ | 194 | 163   | 135   | 194   | 103   | 76    |
| 1,3-Benzenedicarboxylic acid, dimethyl ester | 1525 | C₁₀H₁₀O₄ | 194 | 163   | 135   | 194   | 76    | 103   |
| 1,2,3-Benzentricarboxylic acid, trimethyl ester | 1806.1 | C₁₂H₁₂O₃ | 252 | 221   | 222   | 104   | 149   | 252   |
| 1,2,4-Benzentricarboxylic acid, trimethyl ester | 1845 | C₁₂H₁₂O₃ | 252 | 221   | 119   | 162   | 222   | 252   |
| 1,3,5-Benzentricarboxylic acid, trimethyl ester | 1914 | C₁₂H₁₂O₃ | 252 | 221   | 119   | 252   | 147   |
| 1,2,3,4-Benzentetraacarboxylic acid, tetramethyl ester | 2096.2 | C₁₄H₁₄O₈ | 310 | 279   | 280   | 162   | 104   | 310   |
| 1,2,4,5-Benzentetraacarboxylic acid, tetramethyl ester | 2127.7 | C₁₄H₁₄O₈ | 310 | 279   | 280   | 162   | 75    | 310   |
| 1,2,3,5-Benzentetraacarboxylic acid, tetramethyl ester | 2163.3 | C₁₄H₁₄O₈ | 310 | 279   | 280   | 233   | 162   | 310   |

### Appendix 3. THM-Py-GC–MS marker compounds for proteins

| Target compound name | RI | Formula | MW | Ion 1 | Ion 2 | Ion 3 | Ion 4 | Ion 5 |
|----------------------|----|---------|----|-------|-------|-------|-------|-------|
| Blood – unverified 4 | 1093 | ? | ? | 113   | 56    | 28    | 72    | 131   |
| Benzyl nitrile       | 1145 | C₆H₅N  | 117 | 117   | 90    | 116   | 89    | 63    |
| Blood – unverified 5 | 1336 | ? | ? | 128   | 42    | 127   | 113   | 170   |
| Blood – unverified 6 | 1435 | ? | ? | 128   | 127   | 42    | 57    | 102   |
| Blood – unverified 8 | 1774 | ? | ? | 150   | 165   | 68    | 122   | 94    |
| Blood – unverified 7 | 1815 | ? | ? | 91    | 127   | 42    | 218   | 65    |
| Blood – unverified 9 | 2269 | ? | ? | 139   | 70    | 167   | 42    | 258   |
| Glue – unverified 1  | 1347 | ? | ? | 98    | 42    | 41    | 70    | 114   |
| Glue – unverified 2  | 1474 | ? | ? | 42    | 113   | 156   | 56    | 141   |
| Glue – unverified 3  | 1871 | ? | ? | 198   | 112   | 168   | 44    | 139   |

(Continued)
### Appendix 3. Continued

| Target compound name | RI  | Formula | MW  | Ion 1 | Ion 2 | Ion 3 | Ion 4 | Ion 5 |
|----------------------|-----|---------|-----|-------|-------|-------|-------|-------|
| Blood & glue         |     |         |     |       |       |       |       |       |
| Blood – unverified 1 | 1563| ?       | ?   | 98    | 42    | 41    | 70    | 156   |
| Blood – unverified 10| 1220| ?       | ?   | 55    | 140   | 54    | 56    | 141   |
| Protein 3 – blood & glue | 1702| ?     | ?   | 83    | 168   | 42    | 70    | 112   |
| Tofu & glue          |     |         |     |       |       |       |       |       |
| Protein 4 – tofu & glue | 1423| ?       | ?   | 101   | 88    | 45    | 158   | 172   |
| Tofu & blood         |     |         |     |       |       |       |       |       |
| Protein 1 – tofu & blood | 1725| ?       | ?   | 98    | 42    | 41    | 72    | 170   |
| Egg                  |     |         |     |       |       |       |       |       |
| Indole               | 1307.2| C₉H₇N | 117 | 117   | 90    | 89    | 63    | 58    |
| Egg – unverified 1   | 2196| ?       | ?   | 59    | 72    | 43    | 137   | 202   |
| Tofu & egg           |     |         |     |       |       |       |       |       |
| Protein 2 – tofu & egg | 1350| ?       | ?   | 98    | 42    | 131   | 70    | 160   |
| Protein – various    |     |         |     |       |       |       |       |       |
| L-Proline, 1-methyl-, methyl ester | 1072| C₇H₁₃NO₂ | 143 | 84    | 31    | 42    | 59    | 143   |
| Protein – unverified 7 | 1163| ?       | ?   | 135   | 136   | 134   | 77    | 90    |
| Protein – unverified 8 | 1225| ?       | ?   | 42    | 127   | 142   | 56    | 57    |
| Benzenepropanenitrile | 1246.9| C₉H₇N | 131 | 91    | 131   | 65    | 92    | 77    |
| Protein – unverified 1 | 1495| ?       | ?   | 114   | 43    | 56    | 127   | 155   |
| T-Piperidinopropanenitrile | 1588| C₉H₇N₂ | 138 | 98    | 41    | 204   | 137   | 70    |
| Protein – unverified 3 | 1679.8| ?      | ?  | 128   | 44    | 99    | 42    | 129   |
| Protein – unverified 4 | 1686.7| ?     | ?  | 91    | 155   | 198   | 65    | 213   |
| Glue marker – Mazzeo   | 1740| ?       | ?   | 186   | 93    | 65    | 130   | 65    |
| Blood – unverified 11 | 1274| ?       | ?   | 131   | 130   | 89    | 77    | 132   |
| 1H-Indole, 1,3-dimethyl- | 1371.5| C₉H₁₁N | 145 | 144   | 145   | 102   | 103   | 115   |
| 1H-Pyrole, 1-methyl- | 736 | C₉H₇N | 81   | 81    | 80    | 53    | 42    | 39    |

### Appendix 4. THM-Py-GC–MS marker compounds for carbohydrates

| Target compound name | RI  | Formula | MW  | Ion 1 | Ion 2 | Ion 3 | Ion 4 | Ion 5 |
|----------------------|-----|---------|-----|-------|-------|-------|-------|-------|
| Furfural             | 833 | C₅H₄O₂ | 96  | 96    | 95    | 39    | 29    | 38    |
| Starch – unverified 2 | 1322| ?       | ?   | 87    | 101   | 45    | 115   | 124   |
| Schellmannose        | 1395| ?       | ?   | 101   | 45    | 127   | 71    | 88    |
| Starch – unverified 1 | 1395| ?       | ?   | 101   | 45    | 75    | 127   | 88    |
| Starch – unverified 3 | 1423| ?       | ?   | 101   | 88    | 141   | 73    | 156   |
| Carbohydrate 1 – starch and tofu | 1439| ?       | ?   | 101   | 74    | 45    | 180   | 205   |
| Tofu – unverified 1   | 1457| ?       | ?   | 101   | 45    | 72    | 87    | 218   |
| Starch – unverified 4 | 1530| ?       | ?   | 45    | 89    | 101   | 75    | 161   |
| Glucoside – tofu and carbohydrates | 2234| ?   | ?  | 187   | 101   | 111   | 45    | 219   |
| Starch – unverified 5 | 2544| ?       | ?   | 88    | 45    | 263   | 71    | 175   |
| Laccol carbohydrate – unverified 14 | 1483.5| ? | ? | 129   | 75   | 101   | 161 | 191   |
| Laccol carbohydrate – unverified 1 | 1491| ?       | ?   | 129   | 101   | 45    | 59    | 147   |
| Laccol carbohydrate – unverified 13 | 1497| ?       | ?   | 129   | 75    | 101   | 161   | 191   |
| Laccol carbohydrate – unverified 3 | 1501| ?       | ?   | 129   | 75    | 101   | 161   | 191   |
| Laccol carbohydrate – unverified 2 | 1515| ?       | ?   | 129   | 45    | 101   | 146   | 177   |
| Laccol carbohydrate – unverified 4 | 1526| ?       | ?   | 129   | 75    | 101   | 161   | 191   |
| Laccol carbohydrate – unverified 5 | 1532| ?       | ?   | 129   | 75    | 101   | 145   | 161   |
| Laccol carbohydrate – unverified 6 | 1554| ?       | ?   | 129   | 75    | 101   | 145   | 161   |
| Laccol carbohydrate – unverified 9 | 2457.3| ? | ? | 88    | 101   | 129   | 219  | 75    |
| Laccol carbohydrate – unverified 10 | 2467| ?       | ?   | 88    | 101   | 129   | 219   | 75    |
| Laccol carbohydrate – unverified 7 | 2484| ?       | ?   | 129   | 101   | 201   | 75    | 219   |

Continued
### Appendix 4. Continued

| Target compound name | RI   | Formula | MW   | Ion 1 | Ion 2 | Ion 3 | Ion 4 | Ion 5 |
|----------------------|------|---------|------|-------|-------|-------|-------|-------|
| Laccol carbohydrate – unverified 15 | 2500.8 | ?       | ?    | 129   | 101   | 201   | 161   | 219   |
| Laccol carbohydrate – unverified 8 | 2523 | ?       | ?    | 101   | 129   | 201   | 88    | 219   |
| Laccol carbohydrate – unverified 11 | 2544 | ?       | ?    | 101   | 88    | 59    | 75    | 246   |
| Laccol carbohydrate – unverified 12 | 2570 | ?       | ?    | 101   | 88    | 59    | 75    | 201   |

### Appendix 5. THM-Py-GC–MS marker compounds for natural resins

| Target compound name | RI   | Formula | MW   | Ion 1 | Ion 2 | Ion 3 | Ion 4 | Ion 5 |
|----------------------|------|---------|------|-------|-------|-------|-------|-------|
| Camphor              | 990  | C_{10}H_{16} | 136  | 93    | 79    | 121   | 107   | 136   |
| Camphor              | 1158 | C_{10}H_{16}O | 152  | 95    | 81    | 108   | 69    | 152   |
| Cedar oil            | 1418.8 | C_{15}H_{34} | 204  | 119   | 93    | 105   | 161   | 204   |
| Alpha-cedrene        | 1427.3 | C_{15}H_{34} | 204  | 161   | 204   | 93    | 120   | 147   |
| Beta-cedrene         | 1612.3 | C_{15}H_{36}O | 222  | 95    | 150   | 151   | 207   | 222   |
| Dipterocarpus        | Dipterocarp – unverified 1 | 3278.5 | ?    | ?     | 143   | 191   | 125   | 385   | 367   |
| Dipterocarp – unverified 6 | 3337 | ?       | ?    | 143   | 85    | 109   | 175   | 385   |
| Dipterocarp – unverified 2 | 3352.8 | ?     | ?    | 143   | 99    | 125   | 399   | 424   |
| Dipterocarp – unverified 4 | 3399.3 | ?     | ?    | 143   | 59    | 85    | 107   | 161   |
| Dipterocarp – unverified 3 | 3417.9 | ?     | ?    | 143   | 125   | 413   | 112   | 144   |
| Dipterocarp – unverified 7 | 3440 | ?       | ?    | 143   | 85    | 125   | 161   | 429   |
| Dipterocarp – unverified 8 | 3492 | ?       | ?    | 143   | 191   | 107   | 71    | 383   |
| Dipterocarp – unverified 5 | 3572 | ?       | ?    | 143   | 125   | 85    | 205   | 399   |
| Dipterocarp – unverified 9 | 3572 | ?       | ?    | 143   | 125   | 205   | 399   | 367   |
| Dipterocarp – unverified 10 | 3604 | ?      | ?    | 143   | 125   | 191   | 81    | 383   |
| Benzoin resin        | Benzoin acid, methyl ester | 1126 | C_{8}H_{8}O_{2} | 136  | 105   | 77    | 136   | 51    | 106   |
| Benzaldehyde, 4-methoxy- | 1218 | C_{8}H_{8}O_{2} | 136  | 135   | 136   | 77    | 92    | 107   |
| Benzonic acid, 4-methoxy-, methyl ester | 1354 | C_{8}H_{10}O_{3} | 166  | 135   | 166   | 77    | 92    | 107   |
| 2-Propenoic acid, 3-phenyl-, methyl ester | 1402 | C_{10}H_{10}O_{2} | 162  | 131   | 103   | 162   | 77    | 51    |
| Benzaldehyde, 3,4-dimethoxy- | 1490 | C_{9}H_{10}O_{3} | 166  | 166   | 165   | 95    | 77    | 151   |
| Methyl p-methoxycinnamate, cis | 1683 | C_{11}H_{12}O_{3} | 192  | 161   | 192   | 133   | 89    | 118   |
| Pinaceae             | Methyl neoabietate | 2207 | C_{21}H_{32}O_{2} | 316  | 135   | 316   | 148   | 181   | 257   |
| Methyl pimarate      | 2233 | C_{21}H_{32}O_{2} | 316  | 121   | 180   | 257   | 316   | 301   |
| Methyl isopimarate   | 2346 | C_{21}H_{32}O_{2} | 316  | 241   | 257   | 316   | 187   | 287   |
| Methyl palustrate    | 2354.5 | C_{21}H_{32}O_{2} | 316  | 43    | 149   | 241   | 301   | 316   |
| Tetra decahydro abietic acid methyl ester | 2369 | C_{21}H_{32}O_{2} | 320  | 163   | 123   | 109   | 261   | 320   |
| Methyl-6-dehydrodehydroabietate | 2377 | C_{21}H_{32}O_{2} | 312  | 237   | 312   | 197   | 141   | 165   |
| Methyl DHA           | 2383 | C_{21}H_{32}O_{2} | 314  | 239   | 299   | 314   | 197   | 173   |
| Methyl abietate      | 2384 | C_{21}H_{32}O_{2} | 316  | 43    | 316   | 121   | 256   | 301   |
| Mercucic acid dimethyl ester | 2456.4 | C_{22}H_{32}O_{4} | 364  | 121   | 304   | 305   | 181   | 364   |
| 3-Hydroxy dehydroabietic acid methyl ester | 2461 | C_{21}H_{32}O_{3} | ?    | 237   | 195   | 312   | 41    | 238   |
| Tetrahydroabietic acid, 7-methoxy-, methyl ester | 2481 | C_{22}H_{32}O_{3} | 342  | 342   | 267   | 282   | 227   | 327   |
| Methyl 12-methoxyabiet-8,13-trien-20-oate | 2500 | C_{22}H_{32}O_{3} | 344  | 269   | 344   | 270   | 227   | 329   |
| 15-Methoxydehydroabietic acid, methyl ester | 2545 | C_{22}H_{32}O_{3} | 344  | 329   | 330   | 269   | 313   | 344   |
| 15-Hydroxydehydroabietic acid, methyl ester | 2573 | C_{21}H_{32}O_{3} | 330  | 315   | 255   | 330   | 316   | 237   |
| 7,15-Dimethoxytetradehydroabietic acid, methyl ester | 2611 | C_{22}H_{32}O_{3} | 372  | 372   | 297   | 340   | 313   | 357   |
| 7-Oxodehydroabietic acid, methyl ester | 2624 | C_{22}H_{32}O_{3} | 328  | 253   | 328   | 187   | 313   | 269   |
| 15-Hydroxy-7-oxodehydroabietic acid, methyl ester | 2811 | C_{21}H_{32}O_{4} | 344  | 329   | 269   | 330   | 344   | 187   |
### Appendix 5. Continued

| Target compound name                          | RI   | Formula       | MW  | Ion 1 | Ion 2 | Ion 3 | Ion 4 | Ion 5 |
|-----------------------------------------------|------|---------------|-----|-------|-------|-------|-------|-------|
| Shellac                                       |      |               |     |       |       |       |       |       |
| Butolic acid, 6-methoxy, methyl ester         | 1863 | C_{16}H_{32}O_{3} | 272 | 127   | 159   | 69    | 158   | 83    |
| Butolic acid lactone                          | 1883.9 | ?            | ?  | 85    | 55    | 84    | 113   | 67    |
| Laccijalaric acid, trimethyl isomer           | 2067 | ?            | ?  | 75    | 151   | 306   | 183   | 274   |
| Shellac marker 1                              | 2187 | ?            | ?  | 247   | 187   | 159   | 276   | 306   |
| Shellac marker 2                              | 2197 | ?            | ?  | 247   | 244   | 159   | 187   | 276   |
| Jalaric acid tetramethyl                      | 2206 | ?            | ?  | 75    | 45    | 291   | 304   | 336   |
| Shellotic acid dimethyl ester, dimethyl ether | 2246 | ?            | 352 | 320   | 201   | 228   | 261   | 289   |
| Aleuritic acid methyl ester, trimethoxy       | 2375 | ?            | ?  | 95    | 201   | 71    | 159   | 137   |
| Aleuritic acid, trimethyl isomer              | 2448 | ?            | ?  | 95    | 71    | 145   | 187   | 201   |

### Appendix 6. THM-Py-GC–MS marker compounds for miscellaneous materials

| Target compound name                          | RI   | Formula       | MW  | Ion 1 | Ion 2 | Ion 3 | Ion 4 | Ion 5 |
|-----------------------------------------------|------|---------------|-----|-------|-------|-------|-------|-------|
| Gall                                          |      |               |     |       |       |       |       |       |
| Gall – unverified 1                           | 2984.3 | ?            | ?  | 370   | 147   | 105   | 249   | 213   |
| Gall – unverified 2                           | 3121.6 | ?            | ?  | 94    | 386   | 371   | 148   | 430   |
| Deoxycholic acid, methyl ester, dimethyl ether | 3163.5 | C_{27}H_{46}O_{4} | 255 | 287   | 370   | 355   | 402   |       |
| Gall – unverified 5                           | 3238.8 | ?            | ?  | 253   | 285   | 400   | 368   | 385   |
| Gall – unverified 3                           | 3256 | ?            | ?  | 370   | 355   | 255   | 213   | 402   |
| Methyl 7.alpha.-hydroxy-3.alpha.-methoxy-5.beta.-cholanoate | 3291 | C_{29}H_{44}O_{4} | 420 | 370   | 355   | 255   | 213   | 402   |
| Cholan-24-oic acid, 3,7-dihydroxy-, methyl ester, (3.alpha.,5.beta.,7.alpha.)- | 3344 | C_{29}H_{44}O_{4} | 406 | 370   | 355   | 255   | 213   | 402   |
| Methyl cholate                                | 3394.1 | C_{29}H_{46}O_{5} | 422 | 55    | 271   | 253   | 386   | 368   |
| Methyl hydoexochylolate                       | 3444.6 | C_{29}H_{46}O_{4} | 406 | 55    | 213   | 255   | 370   | 388   |       |
| Sterols                                       |      |               |     |       |       |       |       |       |
| Cholest-5-ene, 3-methoxy-, (3.beta.)-         | 3072 | C_{28}H_{46}O_{4} | 400 | 368   | 400   | 353   | 275   | 385   |
| Cholesterol                                  | 3170 | C_{27}H_{46}O_{4} | 386 | 43    | 386   | 275   | 301   | 368   |
| Cholesta-3,5-dien-7-one                      | 3258 | C_{27}H_{44}O_{4} | 382 | 382   | 174   | 161   | 269   | 367   |
| Tannins                                       |      |               |     |       |       |       |       |       |
| Acetic acid, methoxy-, methyl ester          | 754  | C_{4}H_{8}O_{3} | 104 | 45    | 74    | 29    | 59    | 104   |
| 1,2,3-Trimethoxybenzene                      | 1318 | C_{7}H_{12}O_{3} | 168 | 168   | 153   | 110   | 125   | 95    |
| 1,2,4-Trimethoxybenzene                      | 1377 | C_{7}H_{12}O_{3} | 168 | 168   | 153   | 125   | 110   | 69    |
| 1,2,3,4-Tetramethoxybenzene                  | 1452 | C_{10}H_{14}O_{4} | 198 | 198   | 183   | 140   | 155   | 168   |
| Benzoic acid, 2,3-dimethoxy-, methyl ester   | 1487 | C_{10}H_{12}O_{4} | 196 | 163   | 164   | 196   | 107   | 122   |
| Benzoic acid, 3,4,5-trimethoxy-, methyl ester| 1726 | C_{11}H_{14}O_{5} | 226 | 226   | 211   | 195   | 155   | 183   |
| Arsenic pigments                             |      |               |     |       |       |       |       |       |
| Dimethyl-methylthio-arsine                    | 842.1 | C_{2}H_{4}AsS  | 152 | 137   | 102   | 129   | 121   | 89    |
| Arsenic – As_{4}                              | 1378.9 | As_{4}       | 300 | 300   | 225   | 150   | 75    |
| Arsenic – As_{4}O_{6}                         | 1442.2 | As_{4}O_{6} | 395.7 | 396   | 91    | 289   | 182   | 75    |
| Indigo                                       |      |               |     |       |       |       |       |       |
| Methyl-2-aminobenzoate                       | 1345.5 | C_{6}H_{10}N_{2}O | 151 | 119   | 151   | 92    | 120   | 65    |
| Benzoic acid, 2-(methylamino)-, methyl ester | 1407.4 | C_{7}H_{14}N_{2}O | 165 | 165   | 105   | 104   | 132   | 77    |
| 2-bis-(N-methylindole-3-methoxy)             | 2648.8 | C_{20}H_{20}N_{2}O_{2} | 320 | 320   | 305   | 275   | 290   | 146   |
| Soot                                         |      |               |     |       |       |       |       |       |
| Cadinene                                     | 1417.6 | C_{10}H_{18} | 204 | 161   | 189   | 204   | 105   | 133   |
| Cadalene                                     | 1683  | C_{10}H_{18} | 198 | 183   | 198   | 168   | 153   | 165   |
| Pyrene                                       | 2070  | C_{16}H_{10} | 202 | 202   | 203   | 200   | 101   | 88    |
| Fluoranthene                                 | 2071  | C_{16}H_{10} | 202 | 202   | 203   | 200   | 201   | 101   |
| Indeno[1,2,3-cd]pyrene                       | 3262  | C_{22}H_{12} | 276 | 276   | 138   | 277   | 274   | 124   |

*Continued*
### Appendix 6. Continued

| Target compound name                      | RI  | Formula      | MW  | Ion 1 | Ion 2 | Ion 3 | Ion 4 | Ion 5 |
|-------------------------------------------|-----|--------------|-----|-------|-------|-------|-------|-------|
| **Sulfur markers from minerals & proteins** |     |              |     |       |       |       |       |       |
| Dimethyl sulfide                          | 553 | C₂H₆S        | 62  | 62    | 47    | 45    | 61    | 46    |
| Disulfide, dimethyl                       | 749 | C₂H₆S₂       | 94  | 94    | 45    | 79    | 46    | 61    |
| Dimethyl sulfate                          | 868 | C₂H₆O₂S      | 126 | 95    | 96    | 45    | 66    | 125   |
| **Others**                                |     |              |     |       |       |       |       |       |
| Trimethyl phosphate                       | 968 | C₃H₉O₃P      | 140 | 110   | 79    | 109   | 95    | 140   |
| Caffeine (tea)                            | 1830| C₈H₁₀N₄O₂    | 194 | 194   | 109   | 55    | 67    | 82    |
| Squalene (fingerprints)                   | 2805.5| C₃₀H₄₀      | 410 | 69    | 95    | 121   | 137   | 149   |
| Crown 18 (Anacards)                       | 3028| C₂₀H₂₄O₁₆    | 360 | 121   | 136   | 80    | 360   | 109   |