

FAR EASTERN LACQUERS: CLASSIFICATION BY PYROLYSIS MASS SPECTROMETRY

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1. INTRODUCTION

The scholar is confronted daily with the problems of technology, authenticity and dating of Far Eastern lacquerware. Knowledge of the technology is based on a few antiquarian texts. The usual visual appraisal as an 'authenticity test' quickly reaches its limits when faced with copies, forgeries or even former repairs, additions or restorations, which have been carried out with – as is usual in the Far East – the natural material, Far Eastern lacquer, tapped from *Toxicodendron verniciflua**. Unless the lacquerware has been dated by inscription – which has often been added later – the dating is often made by comparison of style, or by the circumstances of the archaeological find. Up until now, there has been little contribution from archaeometrical investigations for the solution of these problems. This is chiefly due to the complex chemical and physical features of the polymeric Far Eastern lacquer which greatly restrict the analytical possibilities.

2. HISTORICAL BACKGROUND

Ishimatsu (1882), Yoshida and Korschelt (1883) were some of the first scientists who tackled the chemistry of Far Eastern lacquer. They observed that the chief component of the lacquer hardens in the presence of atmospheric moisture, oxygen and, in particular, under the influence of a substance unknown at that time. This substance was identified by the work of Bertrand (1897) to be an enzyme, laccase. These observations, and the work of Tschirch and Stevens (1905) on the chemical composition of the Far Eastern lacquer, formed the foundation for future research. The extensive investigations of Majima *et al.* (1922) on the chief component of the lacquer, which Miyama (1908) named urushiol, lead to the conclusion that urushiol is a mixture of 3-substituted catechol derivatives containing various side chains. Both the structure of the side chains, which was postulated by Majima, and the degree of unsaturation were subjected to a critical revision in the early nineteen-fifties by Sunthakar and Symes (1954) (figure 1). The investigations of Kumantani *et al.* (1976, 1978, 1979) partially elucidated the polymerisation process of monomeric urushiol to the highly polymerised lacquer films of excellent quality. In addition to the enzymatically controlled polymerisation of urushiol, illustrated in figure 2, the polymerisation of the polysaccharides present in small quantities (5-7%) is discussed. With the present level of knowledge of the polymerisation and hardening

* The author prefers the use of the correct systematic name, *Toxicodendron verniciflua*, for the Far Eastern lacquer tree. It is usual to find the designation *Rhus verniciflua* or *Rhus vernicifera* in the literature.

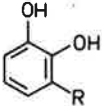
Urushiol		65 - 70 %
	$R = (CH_2)_{14} - CH_3$ $= (CH_2)_7 - CH=CH - (CH_2)_5 - CH_3$ $= (CH_2)_7 - CH=CH - CH_2 - CH=CH - (CH_2)_2 - CH_3$ $= (CH_2)_7 - CH=CH - CH_2 - CH=CH - CH=CH - CH_3$	
Laccase (Cu - enzyme)		1 %
Water		20 - 25 %
Polysaccharides		5 - 7 %

Figure 1 Constituents of the raw, unpolymerised Far Eastern lacquer, tapped from *Toxicodendron verniciflua*.

phases of the lacquer, it is assumed that there is an additional reaction of the polymeric urushiol with the polysaccharides to form a three-dimensional structure. And finally, some of the archaeological investigations made by Kenjo (1973, 1976b and many others) have added not only to the knowledge of the hardening process of the Far Eastern lacquer, but also to the ageing process of the hardened lacquer.

3. ANALYTICAL POSSIBILITIES

In recent years a few papers have been published which deal mainly with the technical and manual aspects (such as construction) of Far Eastern lacquerware and its pigmentation (Garner 1963, Kenjo 1979, Burmester 1982 b). However, neither the investigations of the pigmentation nor of the construction can solve the aforementioned problems*. Rather, as an addition to the above work, a thorough investigation of the organic polymer, i.e. the lacquer itself, seems to be both necessary and promising. However, the structural diversity of the natural polymer, the small lacquer samples – in the order of a few mg – as well as the insolubility in the usual solvents, greatly limit the possibilities of modern analysis. Conventional IR-spectroscopy (Kenjo 1978), Fourier transform IR-spectroscopy as well as solid-state high resolution nuclear magnetic resonance (Burmester 1982 a) have produced little useful information. However, thermolytic or pyrolytic decomposition of the polymeric organic matrix does seem more promising. The disadvantages of thermal analysis of lacquer films (Sato 1963, and Kenjo 1976 a) – low sensitivity to small changes in the molecular structure, and little information on the decomposition processes and products – can be balanced out by the use of pyrolysis

* 'It seems likely that technical studies of pieces of lacquer may help to throw light both on the date of manufacture and the provenance of a piece' (Garner 1963, p. 84).

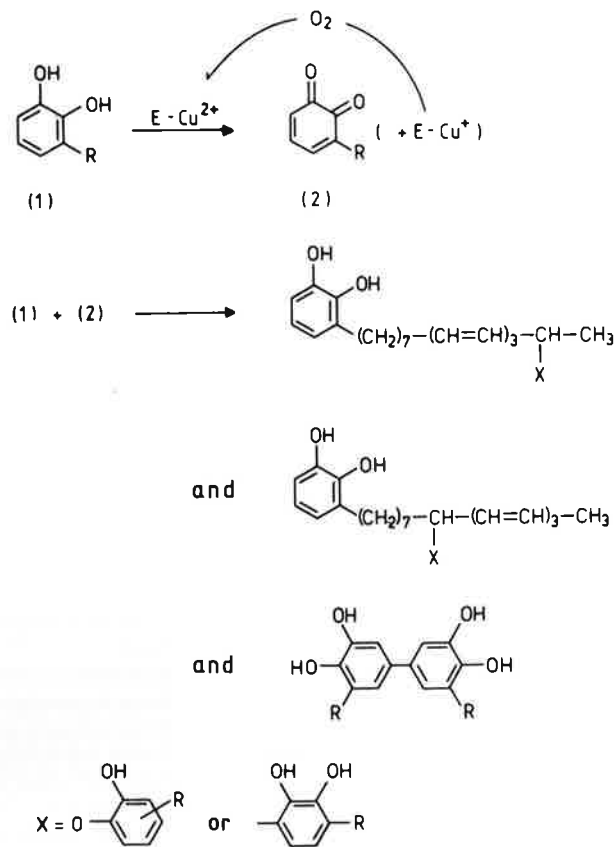


Figure 2 Polymerisation scheme as far as various dimers (according to Kumanotani (1979)). $E-Cu^+$ and $E-Cu^{2+}$ are oxidation states of the copper-enzyme, laccase. R as in figure 1.

mass spectrometry (Py-MS). Py-MS promises not only abundant information on the decomposition products themselves, but also on the decomposition processes in relation to the time in which the decomposition takes place, and last but not least, it will hopefully allow inferences to be made about the molecule before pyrolytic decomposition.

4. SAMPLE PROVENANCE

All the investigated lacquer samples were taken from lacquerware in the Linden-Museum, Stuttgart (West Germany). Preference was given to dated lacquerware of Chinese origin (table 1).

Table 1 *Tabulation of the 47 investigated Far Eastern lacquer samples. All are of Chinese origin, unless otherwise stated. The dates and inventory numbers for samples 5 – 47 were supplied by the Linden-Museum Stuttgart, West Germany*

<i>Inventory no.</i>	<i>Date</i>	<i>No. (*)</i>	<i>Remarks</i>
6RL1	1979	1(A), 2(A)	Modern, unpigmented lacquer, hardened under laboratory conditions. Origin unknown. No organic additives.
6RL3	1979	3(B), 4(B)	Modern, pigmented lacquer, hardened under laboratory conditions. Origin unknown. No organic additives.
9:645B	2nd half 19th c.	5	Japanese
OA 20.787L	1775	6	Dated by inscription
OA 20.804bL	2nd half 18th c.	7	
Stiftung Stoller, gu	1736 – 1795	8	Dated by inscription
OA 20.748L	late 17th/early 18th c.	9	Restored table
OA 20.765L	17th c. ?	10(N)	Black-lacquered interior
		11(N)	Carved, red-lacquered exterior
OA 20.819L	1573 – 1619	12(G)	Dated by inscription, top layers
		13(G)	Lower layers
OA 20.756L	1592	14	Dated by inscription
OA 20.807L	1586	15(D)	Dated by inscription, upper lacquer layers
		16(D)	Base layers
OA 20.813L	1586	17	Dated by inscription
OA 20.763L	2nd half 16th c.	18(O)	Black-lacquered interior
		19(O)	Carved, red-lacquered exterior
OA 20.817L	16th/17th c. ?	20(E)	Japanese?, upper lacquer layers
		21(E)	Base layers
OA 20.796L	1522 – 1566	22	Dated by inscription
OA 20.761L	1522 – 1566	23(F)	Dated by inscription, upper lacquer layers
		24(F)	Base layers
OA 20.753L	1403 – 1424	25	Dated by inscription
OA 20.824L	late 14th/early 15th c.	26(H)	Standing ring of a carved, red-lacquered dish
		27(H)	Decorated upper side
OA 20.825a+bL	1279 – 1368 ?	28(J)	Stand of a bowl
		29(J)	Outer layers
OA 20.848a–gL	618 – 906 ?	30(K)	Undecorated top side of a lacquer painting
		31(K)	Decorated part
OA 20.746L	ca. 12th to 13th c.	32	Japanese ?
OA 20.744L	ca. 8th c.	33	
OA 20.719L	ca. 3rd c. B.C.	34(P)	
		35(P)	Contaminated by the wooden core?
OA 20.730L	1st c.	36	
OA 20.735L	100 B.C. to 100 A.D.	37	
OA 20.736L	100 B.C. to 100 A.D.	38	
OA 20.721L	ca. 2nd half 2nd c. B.C.	39(L)	Interior, contaminated with polyethylene glycol
		40(L)	Exterior, contaminated with polyethylene glycol

<i>Inventory no.</i>	<i>Date</i>	<i>No. (*)</i>	<i>Remarks</i>
OA 20.739A	ca. 5th to 3rd c. B.C.	41	
OA 20.731L	ca. 4th to 3rd c. B.C.	42	
OA 20.720L	ca. 3rd c. B.C.	43(M)	Interior
		44(M)	Exterior
OA 20.722L	ca. 2nd to 1st c. B.C.	45(C)	Base layers
		46(C)	Contaminated with polyethylene glycol
		47(C)	Contaminated with polyethylene glycol

(*) No. refers to the sample number. Samples followed by the same letter in brackets originate from the same piece of lacquerware.

5. EXPERIMENTAL PROCEDURE

The prepared lacquer samples were ground in pro analysi acetone. After evaporation of the acetone, 300 μg were weighed into an aluminium crucible on a micro-balance. The crucible was then closed by a lid with a single hole. The Varian MAT44 quadrupole mass spectrometer, equipped with an electron impact ion source, was operated with an electron energy of 70eV, an emission current of 0.8mA, an ion chamber temperature of 220°C and an accelerating voltage of 2000 V. The sample crucible was introduced into the direct inlet system using a push-rod, and was linearly and reproducibly heated by an externally controlled temperature program. The heating rate was 64°C/min over the range of 25°C to about 350°C. A temperature control was maintained by a thermocouple placed next to the sample crucible. After introduction of the sample and start of the pyrolysis program, the sample was evaporated, the pyrolysis decomposition products ionised, electrostatically accelerated, and analysed in a quadrupole mass filter according to their mass-to-charge ratio, m/Z (m denoting the molecular weight, and Z the electron charge). The mass spectral patterns were observed by scanning repetitively with a scantime of 6 s from m/Z 40 up to m/Z 749. In the course of the pyrolysis, five complete mass spectra were stored in the internal data bank. Because of the long scan time, the corresponding pyrolysis temperatures can only be given to within $\pm 6^\circ\text{C}$ and are: 116, 164, 214, 262, and 311°C. All the collected data had to be punched on cards due to the lack of an interface between the data system of the MAT 44 mass spectrometer and the large calculating unit (Cyber 170 of the Technische Universität Berlin) required for further treatment of the data. This extremely time-consuming step meant that only a small number of lacquer samples could be included in this investigation. Because of the quantitative character of the experiment an idea and quantification of the possible sources of error would be useful. With regard to this, the ideas of Millard (1978, p. 39) were employed, which, because of the fore-mentioned difficulties with the data transfer, have not yet been followed through, but are still being treated. According to Millard, the overall error results from sample handling, irregular evaporation, effects caused by changes in the ion source parameters (mainly temperature and thresholding), measurement accuracy, ion statistics and errors in data acquisition.

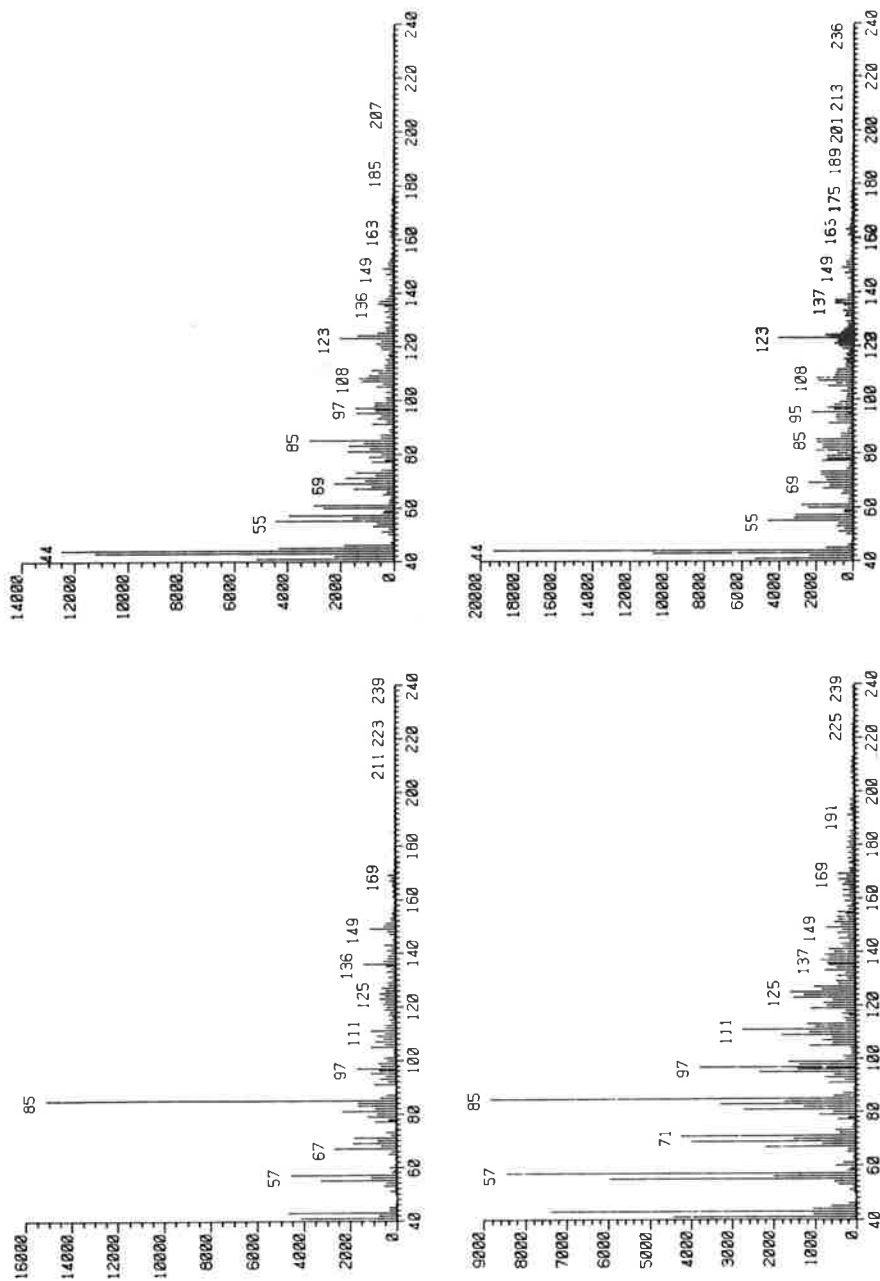


Figure 3 Typical pyrolysis mass spectra (EI, for the experimental conditions see text) of Far Eastern lacquer. Top left: pyrolysis temperature 116±6°C, bottom left: 164±6°C, top right: 214±6°C, and bottom right: 262±6°C.

6. MASS SPECTRAL PATTERN CLASSIFICATION

The electron impact mass spectra of urushiol, an alkenyl phenol, show, even in the unpolymerised state, a large number of very different fragmentation ions (Occolowitz 1964). It was therefore to be expected that the pyrolysis mass spectra of the polymer would show a similar, or even greater, complexity. Indeed, the mass spectra include ions of every molecular weight to well over m/Z 300 (figure 3). The remarkable amount of more than a thousand peaks, or data points, per sample excluded an interpretation of the pyrolysis mass spectra using conventional methods. In addition to the abundance of data, the superposition of several fragmentation processes hindered even simple conclusions about the structure of the polymer before pyrolysis. Although an interpretation of the single spectrum appears to be difficult at the moment, a comparison of the different spectra using multivariate data analysis can be made.

The abundance and also the nature of the data required, first of all, a critical data selection, standardisation, and normalisation. This, and the details of the subsequent multivariate statistical analysis are presented in the appendix. Drastic data reduction was regarded as an essential step, which, with the help of Pearson correlation analysis, ultimately allowed a better interpretation of the mass spectra and a characterisation of each sample with 12 linear combinations. After the identification and the exclusion of a completely atypical sample, 9, different hierarchic classification (figure 4) and iterative relocation procedures were carried out with the help of Wishart's CLUSTAN. The stable classification arrays which resulted were checked with discriminant analysis. In addition, the discriminant analysis indicates that the sample group may be assumed to fall into eight clusters (table 2, and figure 5).

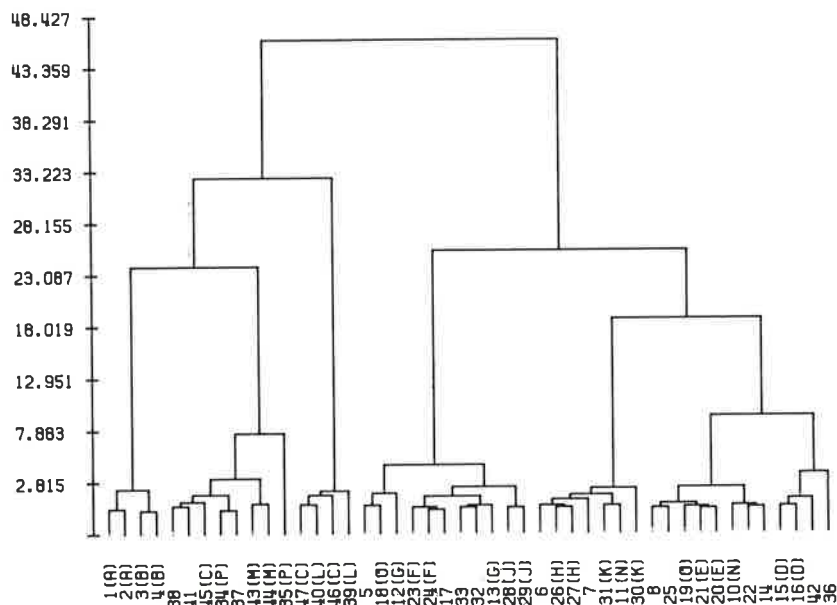


Figure 4 Dendrogram, calculated using Ward's method (optimisation of the error sums of squares). See table 1 for the designations of the samples. In the subsequent relocation procedure, sample 12(G) was regrouped.

Table 2 *Sample distribution for the favoured k = 8 level. Samples followed by the same letter in brackets, originate from the same piece of lacquerware (see table 1).*

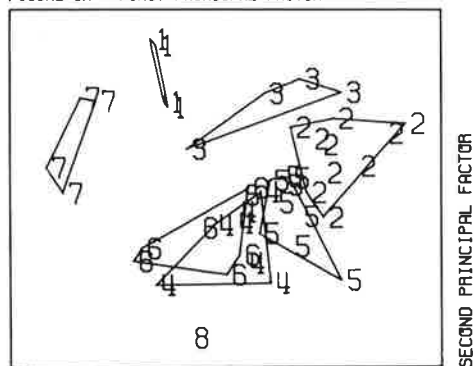
<i>Cluster-number</i>	<i>Sample numbers</i>
1	1(A), 2(A), 3(B), 4(B)
2	5, 13(G), 17, 18(O), 23(F), 24(F), 28(J), 29(J), 32, 33
3	15(D), 16(D), 36, 42
4	6, 7, 11(N), 26(H), 27(H), 30(K), 31(K)
5	8, 10(N), 12(G), 14, 19(O), 20(E), 21(E), 22, 25
6	34(P), 37, 38, 41, 43(M), 44(M), 45(C)
7	39(L), 40(L), 46(C), 47(C)
8	35(P)

7. RESULTS

The multivariate statistical evaluation of the pyrolysis mass spectral measurements of the 47 lacquer samples gave the following results:

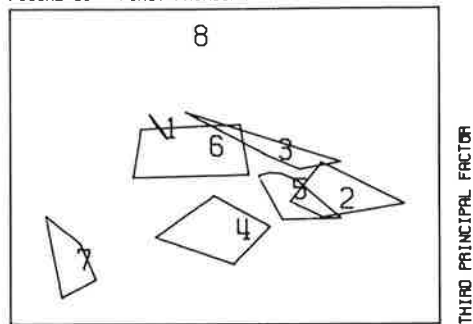
- (1) The following show a high statistical similarity:
 - (a) *all* measurements which were repeated, such as 1(A) and 2(A), 3(B) and 4(B) as well as 46(C) and 47(C),
 - (b) the spectra of lacquer samples which were prepared from directly superimposed lacquer layers (15(D) and 16(D), 20(E) and 21(E) as well as 23(F) and 24(F); the only exception is 12(G) and 13(G)),
 - (c) lacquer samples which originated from one lacquer work, but from two clearly separated areas: 26(H) and 27(H), 28(J) and 29(J), 30(K) and 31(K), 39(L) and 40(L), as well as 43(M) and 44(M); with two exceptions: 10(N) and 11(N) as well as 18(O) and 19(O).
- (2) Unpigmented and pigmented modern i.e. unaged lacquers, hardened under laboratory conditions, form a clearly separate group (1).
- (3) A small group of lacquerware which had been previously treated with polyethylene glycol separated out (appendix, group 7). Indeed, this group 39(L), 40(L), 46(C) and 47(C) still show clear similarities to the remaining early lacquers in group 6 (see also figure 4), however, the spectroscopic results were plainly adulterated. The fact that this group would otherwise have been assigned to group 6 is shown by sample 45(C), which has been assigned to group 6. This sample was prepared from the base layers of a piece of lacquerware, and was obviously not soaked in the conservation agent.
- (4) Remarkably, the results of the grouping approximately follow the dating of the pieces — as far as they are known. This observation is especially clear with group 6, the early lacquer paintings, as well as with groups 2, 4 and 5, the later, carved lacquerware. However, the non-uniformity of group 3 should also be mentioned.

FIGURE 5A • FIRST PRINCIPAL FACTOR



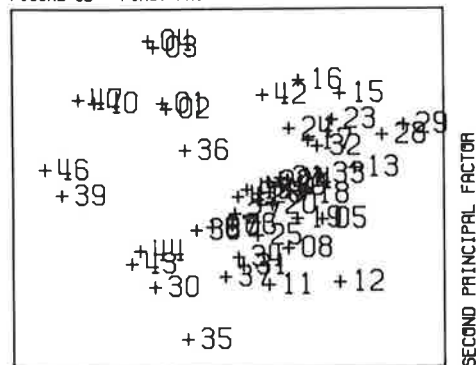
SECOND PRINCIPAL FACTOR

FIGURE 5C • FIRST PRINCIPAL FACTOR



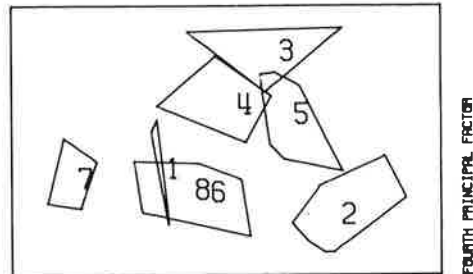
THIRD PRINCIPAL FACTOR

FIGURE 5B • FIRST PRINCIPAL FACTOR



SECOND PRINCIPAL FACTOR

FIGURE 5D • FIRST PRINCIPAL FACTOR



FOURTH PRINCIPAL FACTOR

Figure 5 Optimised distribution of the eight clusters, plotted in the space spanned by the first four principal factors. The cluster outlines connect the outermost samples of each cluster. The numbers relate to the cluster number (see table 2) (figures 5a, 5c and 5d). (a) The distribution of the eight clusters in a plot of the first principal factor (cumulative variance 32%) against the second (cumulative variance 22%). Note the clear separation of groups 1 ('modern lacquers') and 7 (lacquers contaminated with conservation agent). (b) The scatter diagram corresponding to figure 5a. The labels relate to the sample numbers, see table 1. (c) The plot of the first principal factor against the third (cumulative variance 17%). Note the separation of groups 4, 5 and 6. (d) The plot of the first principal factor against the fourth (cumulative variance 12%) shows the significant separation of group 6, the older lacquers, from the four groups of more recent lacquers.

8. DISCUSSION

Due to the aforementioned difficulties, only a small, but well chosen number of samples of predominantly Chinese lacquerware from two and a half thousand years could be included in the investigations. Because of this, and reasons connected with the difficulties of multivariate statistics, care must be taken with the interpretation and evaluation of the results. With the present level of investigations, a purely qualitative evaluation of the experimental procedure shows that the Py-MS is less sensitive to the cited sources of error and influential factors than at first supposed. It seems, for example, that pigments or inorganic additives, such as primer, have little influence on the mass spectral result, and therefore probably

correspondingly little on the polymerisation and hardening of the lacquer. Certainly it is unsatisfactory that the fragmentation processes which produce the pyrolysis mass spectra are not understood; however if the mass spectra are regarded as 'finger prints' of each lacquer sample, and are submitted to the proposed evaluation process, then they allow conclusions to be made, which, with the methods of previously applied analysis, have been extensively unobtainable.

The great similarity of the lacquer samples which have been taken from one object – regardless from which area or lacquer layer – indicates that the lacquer work was usually produced using lacquer 'from one pot' or at least the lacquer originated from one source. If this observation is taken as the rule – the exceptions are discussed later – then a whole series of interesting perspectives are opened up for the investigation of Far Eastern lacquerware. For example, the question as to what extent several parts of a lacquer work form one creative unit. Also, it allows, with high probability, the recognition of additions, repairs and restorations; this has special importance because this kind of work is, as a rule, carried out with original Far Eastern lacquer and not with non-lacquate material. However, the restoration work on sample 9 is an exception to this rule. The two other cited exceptions, 10(N) and 18(O) are from the black-lacquered interiors of two pieces of carved lacquerware of the sixteenth/seventeenth century. These two exceptions did not fall together, as was expected, with 11(N) and 19(O) from the corresponding carved, red-lacquered exteriors. These anomalies in the analytical results can be explained by an addition and repair, since it is known that with works of this period, which were set aside for use, the simple, black-lacquered interiors would have been repaired with the original lacquer when necessary.

A further important point to be stressed is that the methodology is able to recognise non-lacquate materials (9, see appendix), lacquers affected by conservation materials (group 7, see appendix), and modern, i.e. unaged lacquers (group 1). This will, in all probability, have importance in the identification of copies in addition to the aforementioned aspects.

But what is the explanation for the fact that, in addition to the effects described above clearly separated groups can be found? The answer to this may possibly lie in the lacquer preparation and workmanship (technology). Also the part played by the composition of the raw material, which is dependent on the area of cultivation, time of harvest and age of the lacquer tree, must be discussed, along with the possible influence on the analytical results by additives of an organic nature (drying oils) in the case of carved lacquer work (groups 2–5) or by ageing processes of the organic polymer matrix (groups 6–8) by natural ageing or by storage underground prior to excavation (Burmester 1982b).

Although these investigations are still in the early stages, and the results are certainly not completely understood, it can be clearly seen that pyrolysis mass spectrometry in conjunction with multivariate statistical analysis opens a new and promising way of tackling the problems of Far Eastern lacquers.

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* The most important of the Japanese publications which were used, have been translated into German by the Universitätsbibliothek Hannover (Hannover University Library) and the Technische Informationsbibliothek (Technical Information Library), Welfengarten 1B, D-3000 Hannover 1 (West Germany). These publications may be drawn from there under the designation TIB/Ü

APPENDIX

1. Data pretreatment

Because of the abundance of data, the (n, m, t) -raw data matrix (n = samples, m = masses, t = pyrolysis temperatures at which the spectra were recorded [$t = 5$]) was simplified by summing up the absolute intensities p_{ijs} :

$$u_{ij} = \sum_s p_{ijs}$$

where ($i = 1, \dots, n$ $j = 1, \dots, m$ $s = 1, \dots, t$).

The peaks m/Z 198–202 and m/Z 204, which were affected by mercury isotopes (cinnabar is a common pigment), were eliminated. A limitation on the peak-range, i.e. m/Z 40 to m/Z 239, proved to be sufficient without any notable loss of information. Also, it seemed sensible to subject the data to a standardisation

$$v_{ij} = \log u_{ij}$$

a normalisation (2- p norm) (Rozett *et al.* 1975a)

$$x_{ij} = \frac{v_{ij}}{(\sum_j v_{ij}^2)^{1/2}}$$

and finally a transformation

$$y_{ij} = x_{ij} - \bar{x}_{ij}$$

with

$$\bar{x}_{ij} = (1/n) \cdot \sum_i x_{ij}$$

2. Data reduction

The factor analysis – here covariance to the origin as a data transformation, principal factor analysis (part of the SPSS program package), varimax rotation – for the classification of different mass spectra (following the ideas of Rozett *et al.* (1975a, b, 1976)) gave a first, somewhat rough impression of the nature of the samples and the quality of the experiment. The distribution of the samples was defined by the separation of sample 9 as well as samples 39(L), 40(L), 46(C) and 47(C). A careful check of the sampling showed that sample 9 had been taken from an area which had been restored with an unknown material, and the latter samples were contaminated by conservation agent, polyethylene glycol, with which the pieces were treated following excavation. Here, the analytical detection of polyethylene glycol confirmed the factor analytical result. The remaining, less clearly separated samples were then subjected to the data reduction, an essential step for the procedure. A Pearson correlation analysis (part of SPSS) showed that many masses of variables are

Table 3 Set of linear combinations $z_r = \sum y_{ij}$, y_{ij} linearly ~~y~~dependent. Only masses (y_{ij}) included in the table were considered in the statistical treatment

z_r	y_{ij} relates to m/Z																					
1	42	54	63	68	69	74	82	83	85	87	97	99	110	111	125	127	140	141	142	155	169	
2	51	53	77	78	79	80	94	108	120	123	124	136	137	174	188							
3	57	70	112	113																		
4	65	93	121	122	132	135	147	148	161	162	175	189										
5	67	81	95	96	109																	
6	76	104	149	167	205	223																
7	84	98	115	116	129	130	143	157	171	185												
8	91	92	105	106	117	118	119	131	133	134	146	159	173	187	215	217	218	219	221	229	230	231
9	232	233	234	235																		
10	139	153	154	156	158	172	186															
11	163	176	177																			
12	164	165	166	178	208	209																
12	179	180	181	191	193	194	195	197	207	210	220											

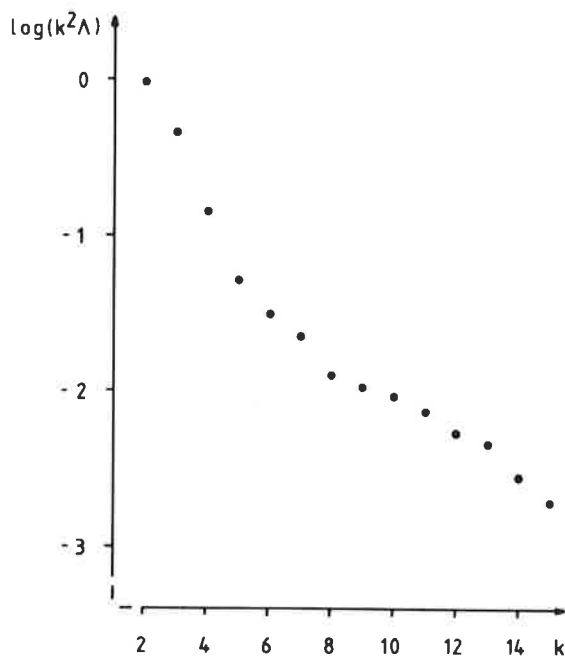


Figure 6 The plot of $\log(k^2 \Lambda)$ (Λ see text) against k (k = the number of clusters) for the determination of the 'real number of clusters', according to Marriott (1971) and Christie (1979).

highly correlated. This positive correlation leads to the assumption that they belong to common fragmentation processes and so the additive combination of these correlated masses to linear combinations (table 3) provides a data reduction. Since all the observed masses originate predominantly from a single, although complicated, macromolecular lattice – built from monomeric units of similar structure – it is understandable that the 12 linear combinations are correlated, even if only weakly, with one another. Thus, the data reduction should serve primarily as a simplification and decoding of the complex mass spectra, the transformation into linearly independent variables is of secondary importance.

3. Classification of the mass spectral patterns

The linear independence of the variables required for the cluster analysis was gained by the use of factor scores. The first five factors were chosen by the criterion of the average eigenvalue (cumulative variance = 92%). With the help of Wishart's CLUSTAN, different hierarchic classifications and iterative relocation procedures were executed (Wishart 1975, Steinhausen 1977). The distance measure used was Euclidian distance. The classification arrays of the hierarchic fusions (Ward's method [figure 4], Lance-Williams flexible strategy, single and complete linkage) as well as a random assignment served as initial distributions for the relocation procedure which followed. The procedure stabilised quickly and global optimal solutions seemed to be reached. A check of the classification results using discriminant analysis permitted, in addition, the use of a method proposed by Marriott (1971) for the determination of the 'real number of clusters'. The plot of $\log(k^2 \Lambda)$ (k = number of clusters, $\Lambda = (\prod_i (1 + \lambda_i))^{-1}$, λ_i eigenvalues, see Marriott (1971) and Everitt (1980, p. 43)) against k (Christie 1979) is given in figure 6, and shows a discontinuity most clearly at $k = 8$. The classification array for this solution is given in table 2. Figure 5 shows the distribution of the samples in a space spanned by the first four principal factors.