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Methods in Organic Archaeometry and their Application to the Terracotta Army

Introduction

Since the 1950s, the application of science to the study of the past is named archaeometry.[1,2] The main tasks of archaeometry are prospection, material analysis and dating. The scientific results ought to be discussed in the context of and together with the disciplines that ask the questions, e. g.archaeology, art history and conservation. This presentation tries to give a survey of methods for organic archaeometry. In this sense, organic archaeometry means the application of scientific methods to organic archaeological objects or residues. These materials mostly originate from natural products, such as oils and fats, waxes, bituminous materials, carbohydrates and cellulotic materials, proteins, natural resins and dyestuffs.[3]

Chemical analysis reveals the composition of a given material and in most cases either serves the identification or the preservation of an archaeological or artistic object. The classical chemical analysis must be considered out-dated and its application to objects of archaeology and art should be avoided. Particularly for organic chemical analysis a too large amount of sample material is required. On the other hand, the exactness of the results is generally low. Similar to infrared spectroscopy, only groups of substances can be found. It is useful to divide instrumental methods for organic analysis into spectrometric identification and substance separation by chromatography. The most prominent methods are shown in fig. 1 together with a very general view over the field of application in archaeology and art.[4]

Fig. 1. Methods of organic analysis and their application to archaeological and art objects (compiled from Mills & White, 1994[3]).

图 1. 有机化学的分析方法及其在研究艺术和考古学中的应用 (Compiled from MILLS & WHITE 1994[3])。

↓ method application to →		oils fats	waxes	bituminous materials	carbohydrate/ cellulotic materials	protein	natural resins	dyestuffs	synthetic resins
Spectrometry									
infrared	IR, FT-IR		v		v	v	v	v	v
nuclear magnetic resonance	NMR	v	v	v			v		v
mass	MS		v					v	
Chromatography: separation									
thin layer	TLC				v	v	v	v	
liquid	LC, HPLC					v		v	
gas	GC	v	v	v	v		v	v	v
Hyphenated methods									
GC-MS		v	v	v	v	v	v	v	
HPLC-UV/vis							v	v	

sample	description	species
M-001/95	rotten wood with soil (scraped)	conifer?
M-002/95	core of rotten beam	conifer?
M-008/95	charred wood relics	family: *Ulmaceae* genus: *Celtis, Zelkova, Ulmus* (elm)
M-009/95	charred wood relics	family: *Pinaceae* genus: *Picea* (spruce), *Larix* (larch)

Fig. 2. Wood relics from Lintong excavation pit no. 2 (Hans-Georg Richter, University of Hamburg).

图 2. 考古挖掘坑道 2 号中的木头残片。

The need of isolated samples is a common characteristic of the majority of organic analytical methods. In the case of the investigation of valuable archaeological and art historical objects of course, this is a severe disadvantage. However, many methods nowadays require only tiny samples of some nanograms, an amount which can hardly be seen by the bare eye. Thus, the sampling technique is the most important step of analysis, when the care of the object is concerned.

Some of the methods discussed here have been applied to problems of the Lintong Terracotta Army in the joint research programme by a number of collaborators.[4] An overview of the results is given here. The investigations focused on the ground layer of the polychromy. This paint layer was found to be mainly responsible for the conservation problems of the polychromy on the Terracotta Warriors, due to its extreme sensitivity to changes in humidity. Some of the scientific results of the joint research programme are published in greater detail elsewhere.[5]

Microscopy

Optical Microscopy

Light microscopy was probably the first technical tool for investigating works of art and archaeology. It is yet today an important method. By light microscopy magnification up to 1500 times is possible. Transmittant illumination techniques as well as top light illumination are commonly applied in the arts and archaeology, using a great number of different technical setups and certain optical effects.

Identification of Fibre and Wood

Polarised light microscopy is a well known transmittant illumination method for the identification of pigments. Furthermore, fibres exhibit optical effects under polarised light as well.[6] These can be used to identify natural fibres from plants as well as from animals. Transmittant light microscopy is also used for botanical identification of wood which is prepared as a thin section.[7]

Application

The Terracotta Army was set up in a giant wooden underground construction. Most of the timber has rotted or been charred. The determination of the tree species from which the timber was produced is of interest for archaeological studies. Two charcoal pieces and two samples of rotted wood from excavation pit no. 2 were botanically determined,[8] as shown in fig. 2. Surprisingly, the charred samples revealed different types of wood. Obviously not much attention was paid to the origin of the wood during construction work.

Stratigraphy

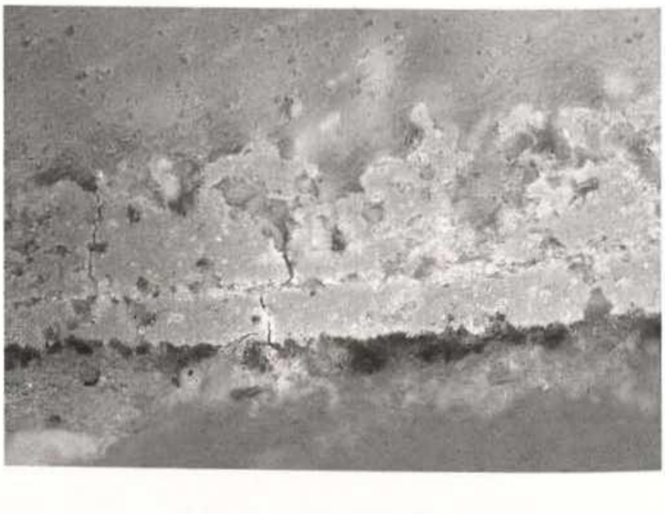
Samples from the surface of an object are commonly prepared as cross sections. In order to investigate their layer structure the polished cross section is examined under the top-light microscope. Some of the layers may appear bright in ultraviolet light due to fluorescence.[9]

Application

The stratigraphy of the polychrome painting layers of the Terracotta Warriors was examined by top light illumination microscopy. Under visible light the ground layer on the Terracotta Warriors looks rather dark and dense. Under UV-light the lacquer exhibits only a weak, greenish-yellow fluorescence.

Fig. 3. Cross section of ground layer on Terracotta Warrior under UV-light (photo: Cristina Thieme).

图 3. 在紫外线照射下的兵马俑表面色彩基层的横切片(图片制作: Cristina Thieme)。



However, here two layers with a total thickness of about 0.1 mm can be recognised (see fig. 3.). Furthermore, the microscopical picture shows a lot of holes and pores in the dryed-out ground layers. In contrast, other examined ground layer samples possess a more dense structure and sometimes also only one layer.

Scannning Electron Microscopy

General

Scanning electron microscopy (SEM) is known as a powerful tool for looking at tiny samples. In the field of art and archaeology magnification up to 10'000 times are common. The particular advantages of SEM cover the field of inorganic material, including elementary analysis. Further advantages of this technique are high magnification and resolution of the topography. Whereas the usual SEM needs totally dry samples, cryo-SEM is capable to visualise damp structures and even water itself. "Cryo" means that sample preparation as well as microscopy are carried out at very low temperatures. Before introducing it into the microscope, the damp sample is shock frozen in melting nitrogen at -210 °C. This allows the water content to solidify into an amorphous state, so that the damp structures are preserved. The investigation itself is carried out at temperatures far below 0 °C, where the partial water vapour pressure lies below the working pressure of the microscope.

Application

Original ground layer samples from the Terracotta Warriors were investigated with cryo-SEM in order to visualise the microstructure of water soaked specimens in comparison to those in dry condition.[10] Fig. 4 shows a double ground layer in damp condition. Two layers can be clearly seen. They exhibit a dense structure and typical brittle fracture forms. Under higher magnification micropores with diameters below 0.1 µm were visible.

Subsequently the cooling of the SEM chamber was stopped and the sample thus dried under the high vacuum. This process led to a total collapse of one of the layers (see fig. 5). This behaviour could probably explain the rolling of the ground paint during drying although this process was much more extensive than under normal pressure. In the remaining layer bigger cavities with diameters above 10 µm have formed. This appearance of the layers closely corresponds to the structure of the air dried ground layer (see fig. 5.).

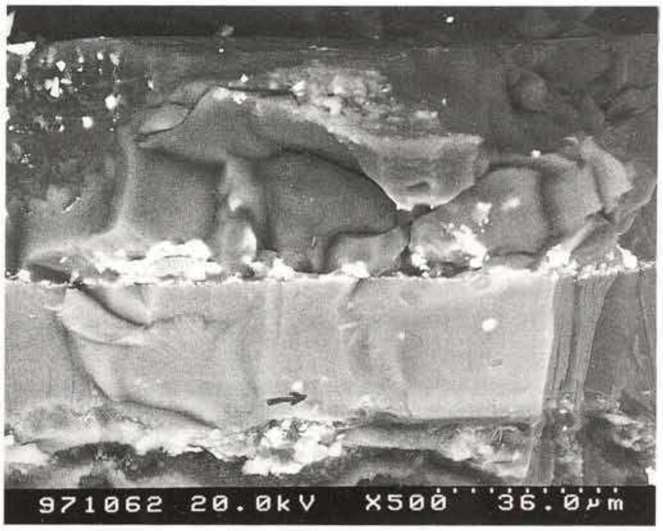


Fig. 4. Cryo-SEM picture of the sectional view of a double "Qin" ground layer in water soaked condition (magnification 500x), (Herbert Juling, MPA Bremen).

图 4. 潮湿的双秦基层截面的低温扫描电子显微图片(放大倍数为 500x)。

Fig. 5. SEM picture of the cross-section after drying in the high-vacuum chamber, magnification 800x (Herbert Juling, MPA Bremen).

图 5. 高真空状态下干燥后的横切片的 SEM 图片(放大倍数为 800x)。

Spectrometry

Introduction

Spectrometry is in general based on the interaction of electromagnetic radiation with the analysed material. Radiation can lose intensity by absorption, reflection, or scattering. A wide range of the electromagnetic spectrum is used for analytical methods. The high energy x-rays are not suitable for organic analysis, but are very useful for elementary analysis by x-ray fluorescence (XRF) as well as for x-ray pictures. For the identification of dyestuffs the choice method is ultraviolet-visible spectrometry (UV/vis). Infrared spectrometry (IR) uses radiation of lower energy than visible light. It is applicable to inorganic as well as to organic substances. The range of radio waves is used for nuclear magnetic resonance spectroscopy (NMR). In this case a magnetic field has to be additionally applied. In a more general sense, the distribution of particles with respect to their mass can be regarded as spectroscopy as well. This principle is used in mass spectrometry (MS).

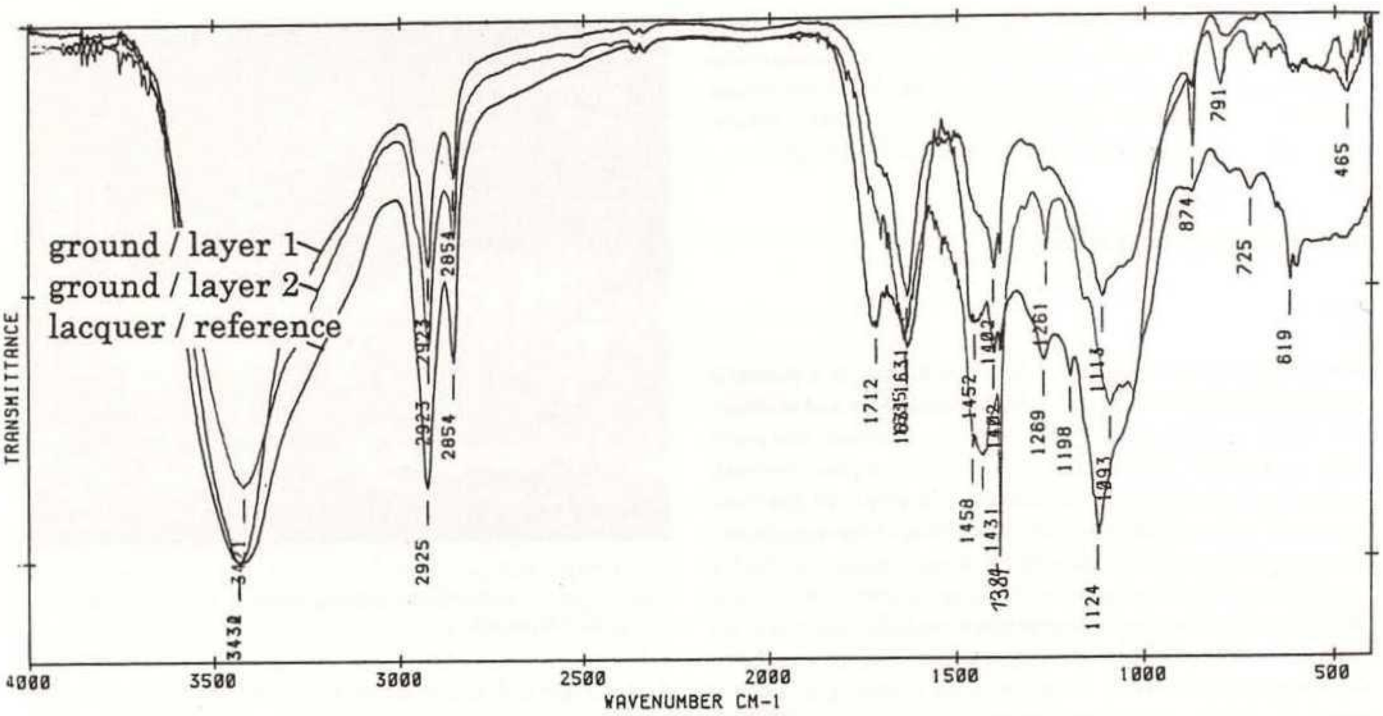


Fig. 6. FT-IR-spectra of ground layers on terracotta fragments and lacquer reference sample (KBr-pellet).

图 6. 兵马俑残片的底色层及参照样品漆(KBr 晶片)的 FT-IR-谱图。

Infrared Spectrometry

General

Infrared spectrometry is based on the absorption of infrared radiation by the chemical bonds in molecules. In an IR spectrum the absorption or transmission is displayed as a function of the energy of radiation and noted as "wavenumber" in reciprocal centimetres. IR spectrometry is applicable to detect a wide range of materials. For pure substances information on the precise molecular structure is obtained. On the other hand, mixtures can be generally characterised only according to the functional groups present. Therefore, in general, it is impossible to distinguish resins, oils or proteins more precisely by IR spectrometry. IR spectrometry is particularly capable for the identification of synthetic polymers. Usually the measured spectrum is compared to reference spectra of known substances.

Nowadays mostly Fourier-transform infrared spectrometry (FT-IR) is used. FT-IR made possible the introduction of microscopy to infrared spectrometry. This technique only requires very small samples in the range of 30 micrometers in diameter or about 30 nanograms of mass. Commonly a so-called diamond anvil cell is used together with this technique. The advantages of FT-IR-microspectroscopy are low sample size, rapid data recording and a wide area of application. Because this technique is non-destructive, the sample once taken may be used for further analysis.

Raman spectrometry is closely related to infrared spectroscopy.[11] Here, the sample or object is illuminated with laser light and the scattered light is recorded. Sample spectra in the infrared range are obtained. Because the scattered light is registered, this technique does not necessarily require isolated samples. Indeed, Raman spectroscopy seems to be the only method up to now revealing information of the organic chemistry of an object without destruction. However, as the Raman effect is very weak, a lot of instrumental problems still have to be solved before Raman spectroscopy can become a routine method of investigating objects of art and archaeology.

Application

In the case of the Terracotta Warriors microchemical test reactions failed in determining the composition of the ground layer. At first by FT-IR it was proved that the ground layer had been prepared from oriental lacquer (Qi-laquer). The FT-IR spectra of the two tested ground layers originating from one fragment show a high degree of similarity to one another as well as to the spectrum of the lacquer reference sample (see fig. 6). By investigation of artificial lacquer samples mixed with different binding media, it was found that the determination of additives to oriental lacquer is hardly possible by FT-IR-spectrometry.

NMR

Nuclear Magnetic Resonance Spectroscopy (NMR) is based on the response of certain atomic nuclei to electromagnetic radiation when exposed to a magnetic field. The most important types of nuclides are hydrogen (^{1}H, proton) and carbon (^{13}C). Each particular type of atom or functional group produces a characteristic signal which is expressed as the chemical shift "delta" in ppm. Furthermore, quantitative information can be deduced from an NMR-spectrum.

Proton- and 13C-NMR-spectroscopy is mainly suitable for determining the structure of organic molecules. In the field of archaeology and conservation NMR spectroscopy has successfully been applied to the identification of resins and ambers, waxes, tar and pitch. Furthermore, the state of decay of wood

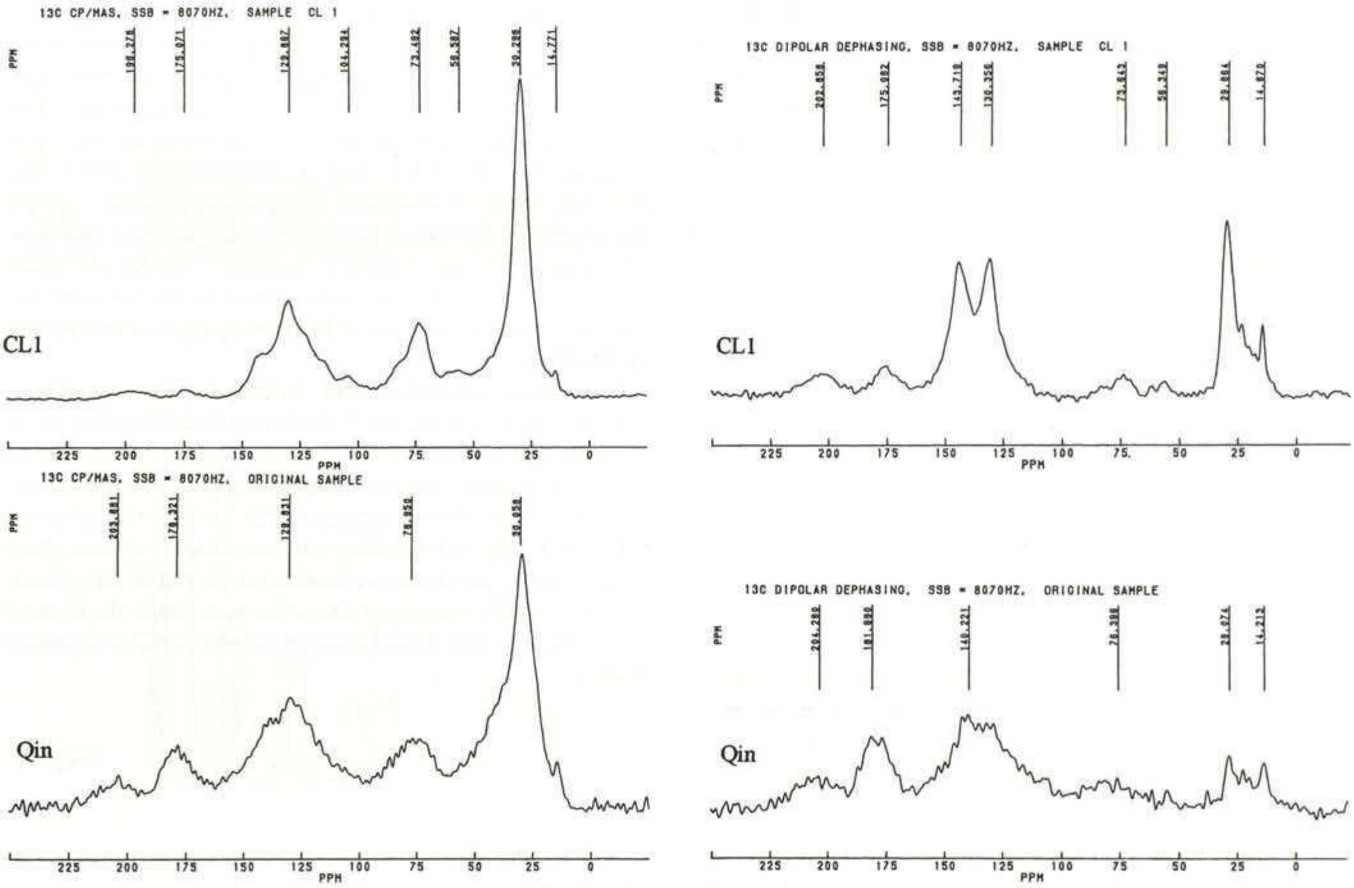


Fig. 7. ^{13}C CP/MAS NMR-spectra of original ground layer sample (Qin) and raw lacquer reference (CL1), (Angelika Sebald, University of Bayreuth).

图 7. 基层底色样品(秦)和原始参照漆的 13C CP/MAS-谱图(CL1)。

and bone has been investigated using this method. More generally, this technique was employed to detect the distribution of water or consolidants inside archaeological objects.[12]

Advantages of NMR-spectroscopy are simultaneous data acquisition and high resolution in discrimintaing functional groups. On the other hand, resolution is poor when investigating mixtures. The former disadvantage of NMR, that only liquid samples could be analysed, has been overcome by special measurement techniques. Solid-state 13C-NMR is performed using cross polarisation and magic angle spinning (13C CP/MAS). Compared to 1H-NMR spectroscopy, the sensitivity of carbon-13 is much lower. This requires longer measuring time and relatively large samples of 50 to 250 mg that need to be powdered. For application in archaeology it is a problem that NMR measurements are strongly disturbed by paramagnetic impurities such as iron salts.

Application

Original ground layer from the Terracotta Army as well as an artificial lacquer sample were measured by solid-stated-carbon-13-NMR.[13] The general shapes of the spectra of both samples are quite similar (Figure 7). This strongly supports the assumption that the ground layer of the Terracotta Warriors consists of oriental lacquer. Differences between the samples can be seen, especially in the content of oxygen-bearing groups (oxygen-bearing aromatic carbons at 145 ppm, carbonyl groups at 175 to 200 ppm). This is attributed to an oxidative weathering of the original lacquer.

Mass Spectrometry

Generally, in a mass spectrometer the analyte is transformed into electrically charged particles. These ions are accelerated and separated according to their mass and their electrical charge. The resulting diagram shows the relative abundance of the particles having a certain mass-to charge-ratio (m/z). It is impossible to present the great variety of MS techniques[14] nor their application on organic archaeometry here. Gas Chromatography e.g. commonly is combined with quadrupol-MS.

In direct temperature-resolved mass spectrometry (DTMS) the sample is vaporised by heating. This method has been introduced to the analysis of resin coatings in the last few years.[15] In contrast to pyrolysis, here the final temperature is reached more slowly, which leads to a separation of low molecular weight parts of the sample from polymeric components. The advantages of DTMS are low sample requirement, short analysis time and no need of sample pretreatment.

Matrix Assisted Laser Desorption and Ionisation (MALDI) is a special method for soft vaporisation and ionisation in MS. It is particularly advantageous for investigation of high molecular and low volatile substances, such as Asian lacquer. MALDI-MS has been applied to some lacquer samples including ground layer of the Terracotta Warriors.[16]

Chromatography

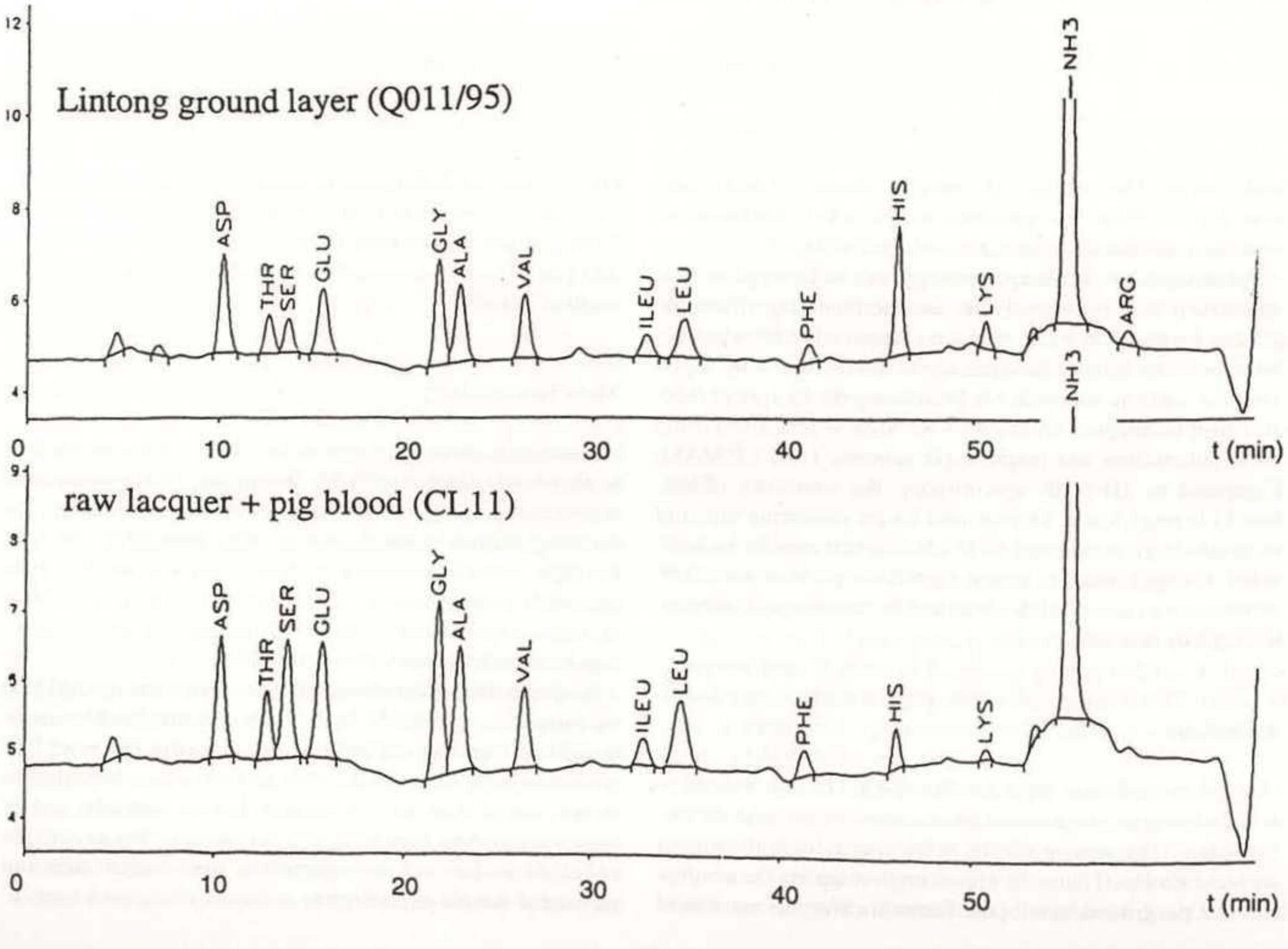
Introduction

Chromatography is a group of analytical techniques for separation, identification and quantification of substances. The common principle is the migration of the substances on the basis of their different distribution on two immiscible phases. One of these is the stationary phase, the other one is the mobile phase. Depending on the arrangement of the stationary phase, planar chromatography can be distinguished from column chromatography. Planar chromatography was begun with paper sheets, later coated glass plates appeared. Now for analytical purposes mostly Thin Layer Chromatography (TLC) is applied using thin plastic or aluminium sheets covered with a finely grained mineral, mostly silica. Planar chromatography has been applied to art and archaeology for almost 50 years, especially for dyes, polysaccharides, resins, and proteins. This method has been revived today in the form of High-performance-TLC (HPTLC) which is characterised by a very thin stationary phase of extremely fine grained particles.[17] In the case of planar chromatography, the separated analyte remains on the stationary phase forming a so-called "internal chromatogram". Each component is characterised by the travelled distance in relation to the front of the moving phase, expressed by the R_f-value.

The column chromatographic techniques, actually using a thin capillary, are commonly further classified depending on the nature of the mobile phase. Different techniques of liquid chromatography (LC) as well as Gas Chromatography (GC) and Supercritical Fluid Chromatography (SFC) have been developed.[18] The column techniques produce external chromatograms, which means that the substances are detected at the end of the column. The resulting chromatogram shows the signal from the detector as a function of time. The characteristic value is called Retention time (t_r).

Fig. 8. Ion-exchange-liquid-chromatograms of: a) hydrolised insoluble part of original ground layer with adherent clay (Q011/95) and b) lacquer reference sample containing pig blood (CL11), (Irene Fiedler, Doerner Institut, Munich).

图 8. 离子交换液相色谱图: a) 带有粘土的原始基层(Q011/95)在水解之后的不溶解的部分; b) 含有猪血的参照漆样品(CL11)。



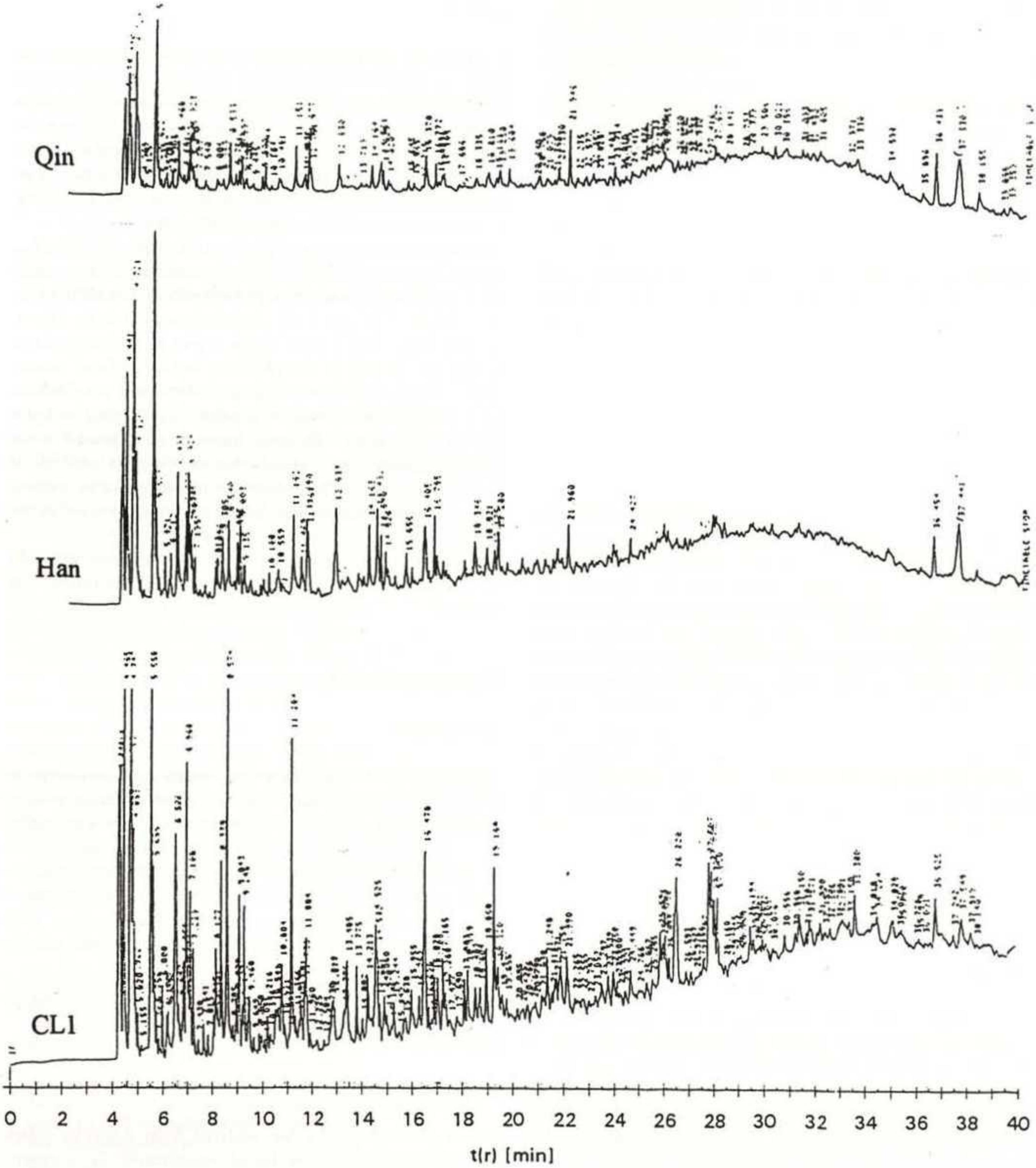


Fig. 9. PyGC chromatograms of original lacquer sample from Lintong ("Qin"), a Han dynasty sample ("Han") and the lacquer reference sample "CL1" Gerhard Heck, Rathgen-Institut Berlin).

图 9. 热解气相色谱图：来自临潼(秦)的原始漆，来自汉代的及参照漆的样品(CL1)。

The material being analysed by a chromatographic technique has to move. Therefore it must be either soluble in the case of TLC and LC or volatile in the case of GC, respectively. Natural polymeric materials (proteins, carbohydrates, dried oils) have to be broken down chemically into their low molecular building units – mostly by hydrolysis in aqueous solution.

Liquid Chromatography

General

Liquid chromatography can be used for the separation of soluble and polar or high molecular substances. High Performance

Liquid Chromatography (HPLC) works with relatively short time spans using high pressure and a thin column. Whereas in the beginning of HPLC the column material was more polar than the solvent, now the most frequently used method is the "reversed phase"-HPLC where the mobile phase is more polar than the column. In the field of archaeometry HPLC is applied to the analysis of amino acis from proteins, dyes, and carbohydrates.

Proteins can be identified by their amino acid composition, which is characteristic for the different types of proteins used as binding media. After hydrolysis of the protein the resulting amino acid mixture is separated and identified by liquid chromatography. A column packed with ion exchange resin is used. In the form of a special "amino acid analyser" this method has been applied to problems in art and archaeology for many years.[19] More recently a HPLC-method for detecting proteins, was described in the literature using special methods of hydrolysis and derivatisation.[20]

Application

Ion-exchange LC was applied to samples of original paint layer of the Lintong Terracotta Warriors as well as to lacquer reference samples in order to detect a possible protein content.[21] It was found that neither the original samples nor the reference contained any water soluble protein components. From the water insoluble residues of two original ground layer samples amino acid profiles were gained, which were similar to that from the lacquer reference sample containing pig blood. This preliminary result hints to the addition of blood to the ground layer painting material of the Terracotta Warriors. Animal glue was not detected in any original sample. However, more original samples as well as different reference material should be analysed in order to confirm this assumption. Contrary to the ground layer, two analysed paint layer samples contained only a few amino acids of low concentration.

Gas Chromatography

General

Gas chromatography (GC) has been used for decades for the separation of mixtures of volatile and low polar components. In this chromatographic technique the moving phase is a gas, while the stationary phase is liquid. In the field of archaeology and art, gas chromatography has been broadly applied to the analysis of most of the organic materials.[3/22] A common way to make the analyte volatile is to treat it chemically, which is called "derivatisation". Another possibility of vaporisation is to decompose high molecular materials by heating, which is called pyrolysis (Py-GC). Successful applications have been reported to the analyses of amber[23] as well as fossile bitumens (jet).[24]

In GC the vaporised sample is forced by means of a carrier gas through a long, thin capillary called "column". The inner surface of the column is filled with the stationary phase, which is a high boiling liquid. Usually, the column is heated. At the end of the column the separated fractions of the sample are registered by the detector. The most commonly used type is the flame ionisation detector (FID). Nowadays, often a mass spectrometer is used as a detector in gas chromatography, as shown below. Like in liquid chromatography, the resulting diagram depicts the time.

Application

In a first step an original sample of the ground layer from the Terracotta Warriors as well as a Han lacquer sample were analysed by GC after conventional derivatisation. Since both samples remained almost completely insoluble only traces of fatty material and of polysaccharides were found without possibility of further identification.[25] This clearly showed that in the case of cross-linked polymers such as oriental lacquer chemical derivatisation is not able to make them volatile.

In the second step pyrolysis gas chromatography (Py-GC) was applied in order to identify the main component in the original ground layer samples as well as in a comparison sample from the Han Dynasty.[26] In fig. 9. the chromatograms of both original samples ("Qin, Han") show a high degree of similarity to one another and are also in accordance to that of artificial lacquer "CL1". Thus it can be concluded that both original samples have been produced from oriental lacquer. The original samples showed fewer peaks with lower intensity as compared to the artificial sample. This suggests that the complex network of hardened lacquer has been degraded or perhaps some components have been leached out during the ageing process in the ground.

Meanwhile, the application of Py-GC combined with MS to asian lacquer has been published in the literature (see below).[27]

Hyphenated Methods

Introduction

"Hyphenated techniques" in general means the combination of two or more separate analytical techniques. Because column chromatography requires external detection, it is particularly useful to combine gas or liquid chromatography with a spectroscopic technique such as UV/visual, infrared, mass or nuclear magnetic spectroscopy. Most of the powerful modern analytical techniques are one of these multi-dimensional systems. They usually are connected to a computer to handle the great amount of data.

HPLC-UV/vis

General

Liquid chromatography has suffered from detectors which are either not highly sensitive or not selective. To overcome this disadvantage, LC is commonly combined with other analytical methods.[28] For the detection of organic dyes in objects of archaeology and art ultraviolet-visible spectrometry (UV/vis) is obviously the best method[29]. After having passed the HPLC-capillary the solution is analysed by the diode-array detector (DAD) which repeatedly generates UV/vis-spectra of the separated substances. The results are normally given as liquid chromatograms. Furthermore, for each retention time a complete UV/vis-spectrum is recorded. So each peak in the chromatogram can be identified by its spectrum, which is typical for certain dyes. The sensitivity of this method for organic dyes lies in the range of a few nanograms.

Application

In the case of the Terracotta Warriors HPLC-UV/vis was employed to samples from pink-coloured parts of the polychromy, representing bare skin. This type of paint was supposed to contain organic dyes because it seemed to bleach out upon being exposed to light after excavation.[30] However, it has to be reported that no organic dye was found in the pink paint layer sample under investigation. Therefore the light-sensitive pink tone is generated by the inorganic pigment cinnabar rather than by an organic dye.[5]

Gas Chromatography-Mass Spectroscopy (GC-MS)

General

Probably the most valuable tool for the analysis of mixtures of low molecular weight organic components has become the online combination of gas-chromatography and mass spectrometry (GC-MS). This is also true for the field of archaeology and art. Numerous investigations of materials from artifacts have been published, including resins, oils, waxes, and proteins.[3, 31]

In this system, the gas chromatograph serves as the separation technique, while a quadrupole mass spectrometer is used for the molecular identification of the components. One great advantage of GC-MS is the capability of detecting extremely small amounts of individual substances in complex mixtures – thus it is ideal for archaeological and artistic works. On the other hand, only volatile substances can be analysed directly. This sometimes requires sophisticated methods of enrichment and pretreatment of the substances to be analysed. Furthermore, the resulting mass spectra are often complicated because of fragmentation of the analyte molecules during ionisation.

From the two-dimensional data resulting from GC-MS set the following diagrams can be deduced:

1. Total Ion Current Chromatogram: For each retention time the signal of all m/z are summed up. Here, the MS just works as a detector similar to the conventional column chromatography.
2. Mass Chromatogram: Here, the intensity for a certain m/z value is plotted over the retention time, so that the occurrence ions characteristic for certain compounds can be extracted from the chromatogram.
3. Mass Spectrum: For a given retention time, the mass spectrum helps identify the compound or structure. An example has been shown before.

py-GC-MS

As already described, polymeric organic material can be vaporised by quick pyrolysis. For analysis of different oriental lacquer samples – however not from the Lintong Terracotta Army – two-step pyrolysis was used prior to GC-MS by Miyakoshi and co-workers.[27] By this means not only the botanical sources of the lacquers could be distinguished, but the polymerisation and crosslinking mechanisms of the lacquer hardening could also be elucidated.

Acknowledegements

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Notes

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9 Bäschlin, N.: *Fluoreszenzmikroskopie*, in: Zeitschrift für Kunsttechnologie und Konservierung (8) 1994, pp. 318-339.

10 The investigations were carried out by Herbert Juling at the Official Materials Testing Laboratory (MPA) Bremen, Germany (report no. MPA 3011/97, 1997). Experimental: mounting of samples (c. 5 mm diameter) on a gripping holder, shock freezing in melting nitrogen (-210 °C), locking in a preparation chamber and breaking perpendicular to the layer. Conductive sputtering with carbon, field-emission SEM, 20 keV, working temperature -130 °C. The pictures were taken in backscattered electron (BSE) mode.

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赫尔姆

有机考古计量学的分析方法及其在研究兵马俑中的应用

简介

自从19世纪50年代以来，一门用来研究过去的应用学科被称之为：考古计量学[1,2]。它的主要任务是：勘探，材料分析和数据处理。科学的分析结论是建立在与考古学，艺术历史及保护科学相互紧密联系，并共地进行讨论的基础上的。这个报告的主要意图是想在有机考古计量学的方法上给出一个全面的观察和研究综述。从这个意义上讲，有机考古计量学意味着一种科学方法的应用，对于在考古对象及挖掘残骸中的有机物的鉴定。这些物质大多数是来自于原始的天然产物，如：油、脂肪、蜡、沥青材料、碳水化合物及纤维素、蛋白质、天然树脂和染料[3]。

化学分析显示出这些材料的物质组成，多数情况下甚至可以帮助用来辨别并保护考古对象和艺术品。经典化学分析方法所提供的数据已经被认为是很陈旧的，所以应该避免继续在考古过程中加以利用。对于大量的样品进行详细地分析是很有必要的，然而另一方面，分析结果的准确度一般来说很低。利用红外光谱只能对物质在种类上加以区分。出于实用的原则，可将有机化学仪器分析手段分成光谱鉴定和物质的色谱分离两部分。图1展示出几种极为重要的分析手段并对它们在研究艺术和考古学中的应用进行了简要的概括[3]。

在大多数有机分析方法中，通常需要隔离样品。但在研究极有价值的考古对象和艺术品的时候，这往往是一个严重的缺点。尽管如此，现今的许多分析方法所需要的样品量，少到只有纳克数量级(ng)。这样少的样品量，是我们很难用肉眼看到的。这样一来，取样技术就成了分析过程中最重要的一步，这直接关系到研究对象的维护问题。

在这里进行讨论的一些方法，是在和许多科技同仁[4]合作研究临潼秦始皇兵马俑过程所应用到的。这里给出的是一个结论综述。这项研究的重点集中在复合彩的基层上。由于这一涂层对湿度的变化极其敏感，所以它对复合彩的保护起着决定的作用。一些在这个联合研究项目所作出的科学结论已经被更详细地发表在其它一些地方[5]。

显微镜检测法

光学显微镜检测法

尽管光学显微镜检测法几乎是在艺术和考古的研究工作中最早使用的技术工具，然而迄今为止，它的重要性仍丝毫未减。光学显微镜检测法的放大倍数可达到1500倍。在利用大量的各种各样的技术装备及特定的光学效应的情况下，无论是穿透照射技术还是表面照射技术的应用都是在艺术和考古工作中极为常见的。

纤维和木制品的鉴别

偏振光显微镜检测法，是一个众所周知的穿透照射法，应用于色素的鉴定。此外，纤维在偏振光下也同样展示出特定的光学效应[6]。这种特性可以用来鉴别自然的动植物纤维。将木制品制成切片样品之后，可使用穿透照射光学显微镜检测法来对它进行植物学的鉴定[7]。

应用

兵马俑被设置在地下很大的木制结构中。其中大部分的木材至今已腐烂或炭化。鉴定这些木材所属树木的种类便成为考古研究的一大主要兴趣。对从2号坑取出的两块木炭和两块腐木的样品，我们进行了植物学的鉴别[8]，如图2。令人惊奇的是，炭化的样品展示出不同的木材种类。很显然，在当初的建造工作中，木材的来源并没有得到很多的重视。

地层学

来自物品表面的样品一般是被进行横截面的制片。为了研究它们层的结构，通常将打光的横截面在表面光照光学显微镜下对其进行研究。一些物质层在紫外线下由于它们的荧光特性而发亮[9]。

应用

兵马俑复合彩的涂层，是通过表面光照光学显微镜检测法进行检测的。在可见光下，兵马俑表面基层的色彩看上去很深很密。但在紫外线照射下，这层漆却显示出微弱的黄绿色荧光。从这里可以辨别出厚达0.1mm的两个涂层(图3)。另外，从显微图片上可以看到在完全干燥的基层上有许多洞和毛细孔。正相反的是，其它被检测的基层样品却拥有较密的结构，而且有时只有一个涂层。

扫描电子显微检测法

概论

扫描电子显微检测法(SEM)是一个用以观察细微样品的有

力工具。在艺术和考古研究领域中，它的放大倍数通常可达到一万倍。在无机材料，包括元素分析的领域中SEM具有特殊的优点。这项技术还具有高分辨率和高放大倍数的优点。然而普通的SEM要求使用完全干燥的样品；使用cryo-SEM (低温扫描电子显微检测法) 能够看到潮湿样品的结构，甚至于水本身。Cryo的意思是指，无论是样品的准备过程，还是显微检测过程，都是在极低的温度下进行的。在将潮湿的样品送入显微镜之前，先将其在液氮(-210 °C)中骤然冷却。在此过程中，样品中所含水的成分处于固体的无定形状态。这样一来，就使得样品的潮湿结构得到了保护。

应用

使用cryo-SEM对兵马俑的原始基层彩进行了研究，用以展示其潮湿的微观结构相对于其干燥的微观结构[10]。图4展示出潮湿状态下的双底色层。在这里，可以清楚地看到两个涂层，它们显示出一个紧密的结构和典型的易裂纹的形状。在高倍显微镜下，可看到它的直径低于0.1 μm。

将真空室的冷却切除后，样品在高真空状态干燥。这个操作过程导致其中一个涂层的彻底毁坏(图5) 。底色在干燥过程中的卷曲或许能够解释这一现象，尽管这一过程要比在常压下进行得更激烈。在幸存的那一涂层上形成了一些直径大于10 mm的孔洞。这一层的出现和被空气干燥的基层结构(见图3)紧密相关。

光谱检测法

简介

光谱检测法通常是建立在电磁波辐射与分析物的相互作用的原理上。电磁波的辐射强度在经过吸收，反射，及散射过程之后会被衰减。在电磁波谱中，很大的波长范围被应用于各种不同的分析手段：高能量的X-射线虽不适合用于有机分析，但对于使用X-射线荧光法(XRF)和X-光片进行的元素分析还是很有用途的。用于鉴别染料可选择紫外-可见光-光谱法(UV/vis)。红外光谱法(IR)使用的辐射能量低于可见光。它不仅可以用来分析无机物，也可以分析有机物质。核磁共振法(NMR，简称：核磁) 所使用的波长在无线电波范围内。在这种情况下要使用外加磁场。从更广泛的意义上讲，不同的粒子，可根据它们质量的不同加以区分。这种因质量不同而引起的粒子分布也同样可以从光谱学的角度来进行处理。这就是质谱法(MS)的原理。

红外光谱法

概论

红外光谱法是建立在分子中化学键对红外线吸收的原理上。在红外光谱中，吸收和透射光强度被作为辐射能量变化的函数，辐射能量由波数给出，单位是cm^{-1}。红外光谱法适用的范围很广。它可用来获得纯净物的准确的分子结构信息；对于混合物可使用官能团的特征表现来进行区分。尽管如此，在通常情况下这种方法却无法用来更精确地鉴别树脂、油、或者蛋白质。红外光谱法有能力来鉴别人工合成的聚合物。通常情况下，将测量的谱图与已知物质的参照谱图进行比较。

现今主要被使用的是经过傅里叶变换的红外光谱法(FT-IR)。傅里叶变换的红外光谱法使得显微镜检测法和红外光谱法的结合成为可能。这项技术只需要直径为30微米，或质量为30纳克的样品量。通常与这项技术一同使用的是一个叫作钻石锻压腔的配件。傅里叶变换红外光谱-显微镜检测法的优点在于：样品需量少，数据处理迅速，应用范围广。由于这项技术不损坏物质结构，所以分析过的样品可以用来作为下一步的分析使用。

拉曼光谱法是很接近红外光谱法的一种分析手段[11]。在这里，分析物在激光照射下所产生的散射光线被进行捕捉和记录。由此而获得的样品谱图可在红外波长范围内。由于所记录的是散射光，所以这项技术不需要使用被隔离的样品。事实上，拉曼光谱法是迄今为止唯一的用来获取物质的有机化学信息而不进行任何结构损坏的分析方法。然而，拉曼效应非常微弱，所以在拉曼光谱法成为艺术和考古研究工作中的常规方法之前，还有很多设备技术上的问题有待解决。

应用

在处理兵马俑的具体问题上，微观化学试验反应在鉴定基层底色的组成上失败了。首先由FT-IR证明：基层底色是来自东方的“生漆”。将从一个基层样品上断裂下来的两个碎片进行FT-IR的测试。这两个碎片的FT-IR-谱图看上去不仅相互间具有高度的近似性，而且和参照样品漆的谱图也极为相似(见图6)。在研究和不同的粘合介质相混和的人工合成漆的时候，发现，对于添加物的鉴定是很难用FT-IR-光谱法来实现的。

NMR

核磁共振谱检测法(NMR)的原理是建立在，当某种特定的原子核暴露在磁场中时对电磁波辐射所产生的反应上。最重要的“核”应数：氢核(^1H, 质子)和碳核(^{13}C)。每个不同类型的原子及官能团都会产生不同的特征信号。这种特征信号用“化学位移”- δ (delta) 的方式表达，其单位为ppm。此外，从NMR-谱图上可获取“定量”的信息。

质子和13C的核磁检测法主要适用于对有机分子结构的鉴定。在考古及维护领域中，核磁检测法曾被成功地应用于鉴定树脂、琥珀、焦油、蜡和硬柏油脂。此外，这种技术手段也已用鉴定木头和骨的腐烂程度。这项技术被更普遍地应用于检测水或加固剂在考古对象中的分布[12]。

核磁检测法的优点在于：测量及数据获取可同时进

行、高分辨率(区分官能团)，但在另一方面，在研究混合物时，其分辨率却很低。以前的核磁只可以分析液体样品。这个缺点如今已被特殊的测量技术所克服：交叉极化和磁角自旋的固态13C-NMR(13C CP/MAS)。与1H-NMR相比，13C-NMR的灵敏度要低很多。这就需要较长的测量时间，和相对较大的样品量：50至250 mg。而且，样品需要事先被粉末化。在考古学应用中出现的问题是：核磁的测量会受到顺磁的杂质如铁盐的强烈的干扰。

应用

对来自兵马俑基层底色的样品及人工漆的样品进行了固态-碳13-核磁法的检测[13]。两个样品谱图的基本形状十分相似(图7)。这就证明了，兵马俑基层底色的组成是来自东方漆的假设。两个样品的不同之处在于含养官能团的含量上(带氧的芳香碳原子的化学位移通常在145 ppm，而羰基官能团的化学位移是175至200 ppm)。这是由于原始样品漆的氧化层所引起的。

质谱检测法(MS)

通常情况下，在质谱仪中的分析物被转化成带电荷的粒子。这些带电粒子在电场中得到加速，并能根据它们本身不同的质量和所带电荷数而被区分开。在因此而得到的谱图上，展示出这些具有一定质荷比(m/z)的粒子的相对丰度。质谱技术种类繁多[14]，展示这些技术及其在有机考古计量学中的应用在这里是不可能做到的。常见的有气相色谱与四极场-质谱结合。

“直接温度解析质谱”(DTMS)中的样品被加热汽化。这种办法在过去曾被用来进进行树脂覆盖层的分析[15]。和高温分解相反的是，这里进行逐渐缓慢的升温至最终温度。这样，便可分离在人工聚合化合物样品中低分子量的化合物。DTMS的优点在于：样品需量少，分析时间短，样品不需要进行预前处理。

“载体支持的激光解析粒子化”(MALDI) 是在质谱法中一个非常和缓的汽化-离子化的方法。这种方法在对高分子量，低挥发性的物质，如亚洲漆，的分析中具有特殊优点。在一些漆的样品，包括兵马俑基层底色的分析中曾使用了MALDI-MS[16]。

色谱法

简介

色谱法是一系列用于物质的分离，鉴定和定量的分析技术。这项技术的基本原理是：物质的迁移，这种迁移是建立在物质在互不相容的两相中的不同分布的基础上的。混合物在层析系统中的分离决定于该混合物的组分在这两相中的分配情况。在这两相中的一相是：固定相；另外的一个是流动相。根据固定相的安装可区分平面层析法和柱层析法。早期的平面层析法使用的是纸片，以后出现了涂有玻璃覆盖层的。目前，出于分析目而进行应用的大多数薄层层析法(TLC)是使用通常表面被极细的硅砂所涂盖的塑料片或铝片。平面层析法在艺术和考古工作中的应用已有近50年的历史。特别是应用于染料、多糖、树脂以及蛋白质。高效薄层层析法(HPTLC)的出现使得原有的分析手段更具生机。这项技术的特征在于，由极其精细的颗粒构成的非常薄的固定相[17]。在分平面层析法中，分析物停留在固定相上，并形成一个所谓的“内部层析”。每一个混合物中的组分都是由它们的相对于流动相前峰行程距离，(由Rf-value来表达)来进行区分的。

在通常情况下，柱层析技术(实际上使用的是毛细管)的种类，是根据固定相的固有特征而进行区分的。在液相色谱(LC)，气相色谱(GC)，以及超晶体流动色谱(SFC)中有很多不同种类的技术得到发展[18]。由柱层析技术所得到的是“外部层析”。它的意思是指，分析物的检测是在柱尾进行的。层析结果是由检测器所显示的信号作为时间的函数来表达的。它的特征值被称为“滞留时间”(t_r)。

在色谱技术中被分析的物质要进行移动，这就要求该物质要么在使用TLC和LC时可溶解，要么在使用GC时易挥发。自然的聚合产物(蛋白质、糖类、干燥的油类)必需使用化学手段进行降解至它们低分子量的结构单元－大多是在水溶液中进行水解。

液相色谱

概论

液相色谱可用于分离可溶、极性和高分子量的物质。高效液相色谱(HPLC)的分析时间短，使用高压，细层析柱。早期的HPLC层析柱所使用的物质要比溶剂更具极性。现今最频繁使用的方法是：逆转相-高效液相色谱。这里的固定相要比层析柱更具极性。在考古计量学领域中，HPLC被用于分析来自于蛋白质的氨基酸、染料及碳水化合物。

蛋白质可由其氨基酸的组成来进行鉴定。不同种类的蛋白质使用其特有的氨基酸来作为连接媒介。蛋白质在水解之后所产生的氨基酸混合物被通过液相色谱进行分离和鉴定。所使用的层析柱的填充物是离子交换树脂。许多年来，这种以“蛋白质分析”为形式的分析手段被应用于解决艺术和考古学科中所出现的问题[19]。一种近来用以检测蛋白质的 HPLC-分析方法曾在一篇文献中得到具体的描述。在这篇文献中使用了特殊的水解和派生方法[20]。

应用

使用离子交换液相色谱来分析兵马俑原始涂层的样品及两个参照漆的样品，其目的在于检测样品中可能含有的蛋白质[21]。结果发现，无论是在原始样品还是参照样品中都不含有水溶性的蛋白质组分。从水不溶性的原始基层残片样品

中得到了氨基酸的结构，这与含有猪血的参照漆样品极为近似。这个初步的结论暗示着，兵马俑的基层涂料中曾被加入了猪血。在任何一个原始的样品中都没有检测到动物胶。尽管如此，还是应该对更多的原始样品及不同的参照材料进行分析，用以证实这个假设。和基层样品相反的是，两个被分析的涂层样品中含有一些低浓度的氨基酸。

气相色谱

概论

气相色谱(GC)在近几十年来被用于分离具有挥发性和低极性的混合物中的组分。在这项色谱技术中，是以气体作为流动相的，其固定相是液体。在艺术和考古学领域中，气相色谱以被广泛地应用于有机材料的分析[3,22]。使分析物气化挥发的常用方法是将其进行化学处理。这就是所谓的“派生法”；另外的一种气化方法是将高分子材料进行加热使其分解，叫做：热解(PY-GC)。关于其成功地应用于分析琥珀[23]和沥青化石(jet)[24]已有报导。

在气相色谱中被气化的样品借助于载气的推动下通过一个又细又长的，被称为“层析柱”的毛细管。层析柱内部表面上装有固定相，这是一种具有高沸点的液体。层析柱在通常情况下被进行加热。在层析柱的末端，可将从样品中分离的组分用检测器进行检测。最常用的检测器的类型是：火焰离子检测器(FID)。目前常使用质谱仪作为气相色谱的检测器，如底下将要进行介绍的。如液相色谱法，气相色谱的结论谱图也是由时间曲线来表达的。

应用

在第一步对兵马俑的原始漆层样品及汉漆样品进行气相色谱的分析之前，使用了常规的派生法。由于两种样品几乎都完全保持不溶解，在没有可能做进一步鉴定的情况之下，只找到了一些油脂物质以及多糖的痕迹[25]。这就显示出，对于交联聚合物，如东方漆的化学衍生物，是无法使其气化的。

在第二步中，为了鉴别兵马俑的原始底层漆样和一个汉代的对照样品[26]中的主要成份，使用了热解-气相色谱(PY-GC)。在 图9中，两个原始漆样(“秦”、“汉”)的色谱图不仅在其相互间展示出的高度近似性，而且与人工漆“LC1”也具有一致性。由此可得出的结论是：两个原始漆样都来自东方漆。和人工漆样品的谱图相比，原始漆样谱图的峰较少，强度较低。这暗示着，对硬化的漆进行的复合网络工作曾被简化，或者，也许样品中的一些组分在地底下的老化过程中有所流失。在此期间，关于使用热解气相色谱法结合质谱法对亚洲漆进行分析的应用已在文献中进行了发表(见下)[27]。

级联的方法

简介

“级联法”一般是指两个或多个独立的分析技术手段的结合。因为柱层析需要外加的检测器，所以气相或液相色谱与光谱技术的结合就更有意义。如，紫外/可见光谱、红外光谱、质谱、及核磁。大多数强有力的现代分析技术都是一种这类的多维系统。它们通常都是与计算机连接用来处理大量的数据。

高效液相色谱-紫外/可见光谱法(HPLC-UV/vis)

概论

液相色谱由于检测器的非高灵敏度，非选择性而受到阻碍。为了克服这个缺点，经常将液相色谱与其它分析手段相结合[28]。对于在考古及艺术领域中有机染料的检测，很显然是紫外/可见光谱(UV/vis)当选的手段[29]：在溶液通过HPLC-毛细管之后，由一个对不同物质重复进行紫外/可见光谱检测的二极管阵列检测器(DAD)将其进行检测。结果一般是由液相色谱图给出。此外，对每一个滞留时间都有紫外/可见谱图的记录。所以在液相色谱图上的每一个峰都可以通过其用来表达某一特定染料的特征光谱图来进行鉴别。这一分析手段的灵敏度可达到纳克级(ng)。

应用

在兵马俑的研究中，高效液相色谱-紫外/可见光谱法(HPLC-UV/vis)被用来进行来自复合色中展示裸露皮肤的粉红色部分的样品的分析。这种类型的涂料猜测可能含有有机染料，原因是，在其出土后暴露在阳光下而似乎完全脱色[30]。然而，在研究中还没有报导过在粉红色层中发现有机染料。尽管如此，与其说这种对光敏感的粉红色陶来自于某种有机染料[5]，不如说它是由无机色素硫化汞矿(朱砂)制成的。

气相色谱-质谱法(GC-MS)

概论

很多有价值的、用来分析低分子量有机组分混合物的分析工具，都是气相色谱和质谱的在线组合(GC-MS)。在考古和艺术领域也是如此。大量的对来自艺术品的材料进行的研究工作已经得到发表，其中还包括树脂、油料、蜡和蛋白质[3,31]。

在这个系统中，气相色谱法作为分离技术，一个四极质谱仪则是用来对各组分进行分子鉴别。GC-MS的一大优点是它对络合混合物中极其少量的个别物质进行检测的能力。这对考古和艺术研究工作是十分理想的。但在另一方面，只有可挥发的物质能够被直接地进行分析。这就需要有时使用高尖端的技术手段对要分析的物质进行浓缩和预前处理。此外，结论中的质谱图经常是很复杂的。这是由

于在离子化过程中被分析分子的断裂而造成的。

从GC-MS 装置而得出的二维数据可推得如下的谱图：

1. 总离子流色谱图：对每一个滞留时间都将质荷比(m/z)信号进行叠加。在这儿，质谱只是作为一个检测器，类似于传统的柱层析法。
2. 质量色谱图：在这儿，质荷比信号强度是在建立在滞留时间的基础上绘制出的。借此，可将某一特定化合物产生的离子特征从色谱图上分离出来。
3. 质谱图：对于给定的滞留时间，质谱可以帮助鉴别化合物或其结构。前面已经介绍了一个这样的例子。

热解气相色谱-质谱法(py-GC-MS)

正如所描述，聚合有机材料可通过热解的办法进行气化蒸发。Miyakoshi 和他的同事们在对不同的原始漆样品(并非来自临潼兵马俑)进行分析时，曾在GC-MS之前使用了两步热解法[27]。使用这种手段，不尽可以对来自于植物的漆进行研究，而且硬化漆的聚合及交联机理也可得到阐述。

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注：

尾注请见英文文本。