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Brown and Black Organic Glazes, Pigments and Paints

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Introduction

This article covers a wide variety of natural products and their modified counterparts. It has been necessary to restrict attention to those organic browns and blacks that are likely to serve as pigments and binders in paintings, prior to the beginning of the twentieth century. Synthetic coal tar dyestuffs developed in the latter part of the nineteenth century are beyond the scope of this article. All of the source materials discussed here occur naturally or are directly derived from animal and vegetable sources by human or geological agency. Some attention is given to carbonaceous materials such as charcoal, even though these are usually characterized by simple microscopy rather than organic analytical techniques. As new techniques with improved sensitivity appear in museum laboratories it should be possible for the organic chemist to take a more active part in the indentification of materials such as carbon blacks.

The Scientific Department of the National Gallery, London, has pioneered the application of instrumental methods such as gas-chromatography (GC) and gas-chromatography–mass-spectrometry (GC–MS) to organic problems involving easel paintings and other art objects [1–11]. These techniques have been supplemented by infra-red spectrophotometry, thin-layer chromatography and, more recently, microbore high-performance liquid chromatography. For this reason no apologies are offered for restricting attention to identifications employing these techniques alone but it should be pointed out that other techniques such as C^{13}–nuclear magnetic resonance (C^{13}–NMR) and electron spin resonance (ESR) have also found application, the latter being particularly useful for coal and carbonized materials such as charcoal [12–14]. On balance, classical tests (wet test) are of relatively limited value. Little of any consequence is readily available to the museum analyst on the subject of these materials and it is

the author's aim to bring together as comprehensive a survey of both firm analytical results and our present understanding of their complex chemistry as may be possible within the confines of space and content set for this article. At the same time it would seem useful to indicate a little of the known history and technology of these materials by including references and recipes for their production or use.

To begin with the taxonomy, we may conveniently divide them into those which are naturally formed, that is by natural and geological forces and those artificially formed, that is manufactured. Table 1 summarizes the main divisions.

Dark-coloured primary products of biosynthesis

Terpenoid resins and balsams: an outline

For the most part these materials are but straw-coloured when freshly formed. As a result of subsequent oxidation and formation of powerful chromophores, they progressively darken. Nevertheless many triterpenoid resins remain little more than pale yellow, some dammars producing films possessing little tint, even after ageing. On the other hand some 'dammars' such as 'black dammar' from *Canarium strictum* (in fact, a member of the Burseraceae whose resins are typically known as elemis) are very dark, even before painting out [15]. In such cases and when mixed with drying oils, even darker films result on ageing. Other resins, such as those from *Liquidambar orientalis* (black storax), from the Hammamelidaceae, give a dark brown coating when applied as a spirit varnish, but these lack lustre and have a tendency to be somewhat inhomogeneous. When ground and after prolonged storage, it loses its characteristic balsamic and spicy odour. This coupled with the tendency for its exposed surfaces to turn black could well have led to some confusion in times past with bituminous materials. It consists of triterpenoids and phenolic esters of aromatic acids [16] such as coniferyl benzoate. Certainly it would incorporate well with drying oil, when methods commonly recommended for asphaltum were employed (see below).

Amongst the diterpenoid resins we must mention the part played by the copaiba balsams in glazing and as a toned varnish. In this context we may single out the copaibas from various *Copaifera* sp. (Leguminosae) found in South America. They were collected as pale yellow mobile oleoresins. On storage or painting out, they darken to a golden through to red-brown colour. Some information is available in the scientific literature on the chemistry of these and similar materials [17–25].

Given that these resins originate in South America and the Caribbean, the former copaibas being the most import-

Table 1 Taxonomy of brown and black pigments.

Primary products of biosynthesis

1. Terpenoid resins and balsams (darkening following formation or on storage)
2. Non-terpenoid resins and balsams

Geologically modified organic material

3. Bitumen and asphalt
4. Pyrobitumens

Artificial products formed by pyrolysis

5. Tars and smoke condensates
6. Pitches

ant, it seems that they were not widely available until the seventeenth century. The Paduan manuscript (late-sixteenth to mid-seventeenth century) makes reference to the use of copaiba as an ingredient of amber varnish, whilst Sheldrake is reported as maintaining that it had been used as a varnish and a paint medium by the later Venetian masters [26]. Reynolds states in his notes: 'Offe's picture painted with *cera* and *cap. solo, cinabro* [. . .]' [27] which is interpreted as: painted with wax and copaiba, vermilion for the red. In reference to his own portrait, Reynolds speaks of first painting with oil and then glazing with copaiba, yellow ochre and lake, with no varnish. This seems to have been altered to, 'painted with lake, yellow ochre, blue and black, *capi.* and *cera vern.*'; that is, wax dissolved in Venice turpentine as varnish used with copaiba. Mention of copaiba as an ingredient in other paint vehicles and glaze/varnish compositions is made in references to several other of his portraits up until the mid-1770s. Thereafter there is no further reference to it. Overall, we are left with the impression that he sought to attain a degree of richness and depth in his painting technique by use of transparent, highly refractive media components, such as the balsamic resins. Moreover one gains the impression that he was in the habit of restricting the main paint layers of his works to the cooler colours, preferring to add warmth and richness by glazes of copaiba and other liquid resins, with or without yellow pigments.

One may observe with interest at this point Charles Eastlake's observation that similar balsams or resins were employed with certain colours by Netherlandish painters and that colours mixed with copaiba would best be diluted slightly with drying oil. The anonymous author of *Traité de la Peinture au Pastel*, dated 1788, advises that copaiba should be used in place of, or slightly diluted by an oil [28]. Fig.1 shows an example of a glaze sampled from Reynolds's *Self Portrait* in the Royal Collection.

Amber varnish: There are many references in the old literature to 'amber varnishes'. It would seem to be made in much the same way as 'run' hard copal varnishes. That is, by heating the resin with strong drying oil at a temperature that causes partial decarboxylation of the resin and the two components are incorporated into a tough, durable but dark varnish.

Technically amber is a true fossil resin, the most widely available in Europe being Baltic amber, found mainly in the 'blue earth' stratum situated in Poland and Lithuania. However as a result of its low density, it is commonly transported by water to other Baltic coasts. Extensive investigations of its chemistry have been made in recent times [29–32]. It is mostly polymer with traces of monomeric terpenoids. Amber varnish recipes are mentioned in various manuscripts and treatises such as the 'Marciana Manuscript' (early- to mid-sixteenth century) and the 'Volpato Manuscript' (late-seventeenth to early-eighteenth century). It would appear that considerable quantities of this varnish were manufactured from fragments and cuttings during the peak production of amber in East Prussia. Fig.2 shows a chromatogram of a prepared amber varnish, aged as a thin film. It had excellent film-forming characteristics, was of a rich brown hue, good gloss and was found to be tough and durable, with no tendency to bloom. The distillation residues of oil of amber are known to have been used as a substitute for the pigment asphaltum (see section headed 'asphaltum').

Miscellaneous non-terpenoid brown resins

Balsams from various *Myroxylon balsamum* varieties of the Leguminosae providing balsam of Peru and balsam of Tolu give dark brown to black liquids, resembling tars. These give rich dark brown glazes in thin-film form. Unfortunately little is known of their chemistry. However they have been reported to contain coniferyl and benzyl benzoate [33]. Fig.3 illustrates a typical chromatogram for an aged sample of balsam of Peru.

Whereas the former balsamic materials are based on benzenoid components, there is another class of resinous substances called gum-resins from the family Burseraceae. These are triterpenoid in part and contain a proportion of water-soluble gum. Though frankincense from various *Boswellia* species and myrrhs from *Commiphora* species have been mentioned in recipes for varnishes, only the latter has a red to brown colour [34,35]. These are mentioned at this point, not because it is thought either would be used on their own as tinted glazes, but in anticipation of their presence in mummy (see below).

Aloes: Several species of the genus *Aloë* yield a coloured juice on cutting the leaves. This is allowed to evaporate and ground to a powder that can be used as a pigment or tint for the production of a glaze or tinted varnish. It has a yellow-brown colour. The main species which produce the better grades are *A. vera* from the West Indies (Barbados or Curaçao aloes), *A. ferox* and *A. perryi* from South Africa. Approximately 25% of the resin consists of barbaloin and small amounts of the C–glycoside of aloe-emodin [36]. Recipes refer to various kinds, Socotrine (red-brown, from *A. perryi*), hepatic (dull brown) and Caballine aloes (black).

Spanish liquorice or Spanish juice: This brown pigment is obtained as a gum extract from *Glycyrrhiza glabra* var. Spanish. *Glycyrrhiza* sp. have been known and used by man for at least 4000 years [37]. Their chemistry appears to be based in part, on prenylated flavanones [38,39].

The aqueous extract, with a little gum gives a rich brown paint, that has excellent film-forming and glazing qualities. Unfortunately it is susceptible to fading when exposed to light. It has been employed to temper other brown and black pigments such as bistre and asphaltum (see below). It was said to, 'supply the place of bistre in a great measure, though it is inferior' [40,41].

Mummy: This pigment consists of the parts of an Egyptian mummy, typically ground up with a drying oil such as walnut. From entries in *A Compendium of Colours* [42], it would seem that the fleshiest parts of the mummy were most highly recommended for the preparation of best quality mummy pigment. In the past it also went under the name of 'Egyptian brown' and it seems to have been mixed with ultramarine, lake pigments and the like, for application as a warm glazing pigment. Moreover it would seem that it has less tendency to cause cracking and crocodiling when mixed in oil than its counterparts, asphaltum or bitumen. Indeed, Field heartily recommends it as a substitute for the latter pigments in his book *Chroma-*

Figure 1 A golden-brown glaze-like layer from Reynold's *Self Portrait,* Royal Collection. The sample had been saponified and methylated prior to analysis. In addition to fatty acid methyl esters (liberated from linseed oil), there are resin acid methyl esters from a conifer source (marked C). Traces of labdane esters (marked L) suggest the presence of resin from a Leguminosae source, most likely copaiba balsam.

Analytical conditions: on-column injection, 25 metre wide-bore quartz capillary column with SE30–equivalent bonded phase; temperature programmed from 110°C to 290°C, at 7°C per minute, helium carrier; 45 eV electron impact mode; 1 second per decade scan rate.
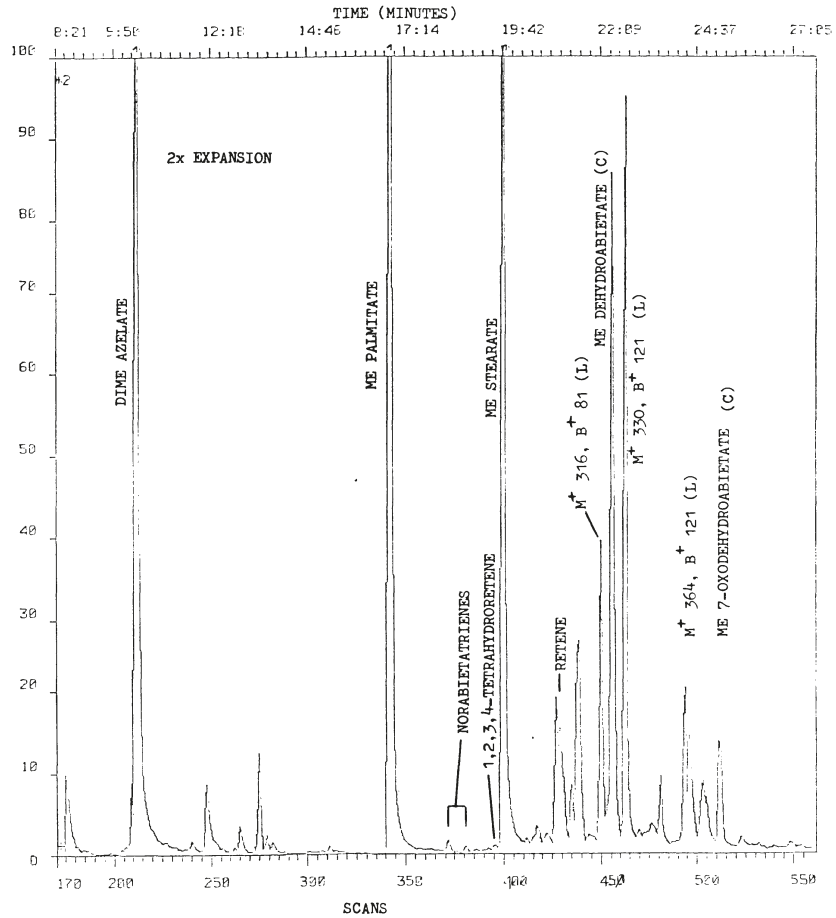
Figure 2 Aged amber varnish film. The varnish was formulated from 'run' Baltic amber and linseed oil, with a minor addition of spirits of turpentine. The chromatogram represents the total ion contribution and the sample was saponified and methylated prior to injection. Because of the very low amounts of terpenoids surviving, the chromatogram is displayed with a four-fold expansion of the ordinates.

Analytical conditions: similar to those employed in Fig. 1.
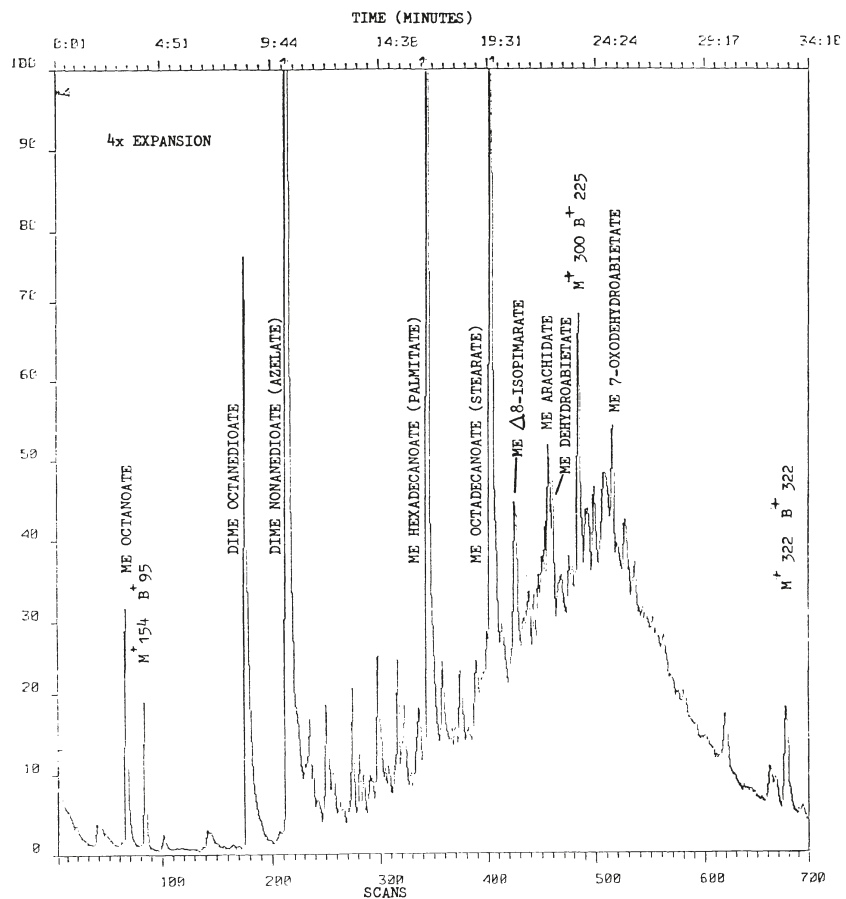
tography [43]. As far as Europe is concerned the history of mummy extended back to the sixteenth century and probably well before, since it was prized as a medicine. Despite a ban on the shipment of mummified bodies from Egypt during the sixteenth century, it is known that it was still a lucrative source of trade for the Arabs.

It is a very difficult material to characterize chemically and it is rarely likely to be firmly identified in actual paint samples other than under exceptional circumstances. Since the Twelfth Dynasty, mummies have been dark-coloured and on occasions completely black. On balance, opinion has it that bitumen and bituminous materials were not used appreciably before the Ptolemaic period and even then for the less important cadavers otherwise, according to Coremans [44], the Egyptians much preferred resins. One must conclude that colour has caused much of the confusion and this has been compounded by the fact that medieval Egypt carried on a substantial trade in *mumiya*, which stood for 'wax' in Persian, and 'bitumen' in Arabic. It seems that only at a later date did this term come to stand for the scrapings of mummy linen or the ground-up contents of the body cavities, which were sold as a drug. Ibn al-Beitar records that:

Mumiya is the name given to the drug just mentioned and to the bitumen of Judea and to the mumiya of the tombs as found in great quantities in Egypt and which is nothing else but the mixture formerly used for embalming the dead, in order that their dead bodies might remain in the state in which they were buried and neither decay nor change. [45]

As far as can be determined, this material arrived in west-

ern Europe by the twelfth century and possibly earlier. It was used both in paints and in medical prescriptions, but trade in this commodity seems to have almost died out by the end of the seventeenth century.

Historical evidence for its constitution is shaky and confused to say the least. Only Diodor and Strabo refer to the use of bitumen in mummification. The word for 'preserved body' (*qasiu* or *qas*) certainly gives no indication at all, that bitumen was employed in the process. Certainly Lucas and Spielman concluded from the available evidence that bitumen would not seem to have been used to any great extent prior to the rule of the Ptolemies and, moreover, the latter opined that it was not introduced into the mummification practice until the XXII Dynasty (*c*.945–715 BC). During the Graeco-Roman period, bitumen fishery in the Dead Sea assumed considerable importance to Egypt. Medical papyri such as the 'Rhind Papyrus' give an indication of the use of fats and resins. Thus [46]:

Anubis . . . fills the interior of the skull with mrhe Hr, incense, myrrh, cedar oil and calves' fat.

So it would seem reasonable that we should be able to distinguish mummy from bitumen and asphaltum in favourable circumstances, since by all accounts the former should consist of a complex mixture of resinous adhesives, proteinaceous materials from the flesh — that is a form of gelatin — as well as the materials from the mummy wrappings. Gum arabic from *Acacia* sp. has been identified in samples of mummy [47]. Investigators at Manchester have found by thin-layer chromatography, gas-

Figure 3 Balsam of Peru (*Myroxylon* sp.), aged film. The ether extract was methylated and examined under the analytical conditions outlined in Fig. 1.
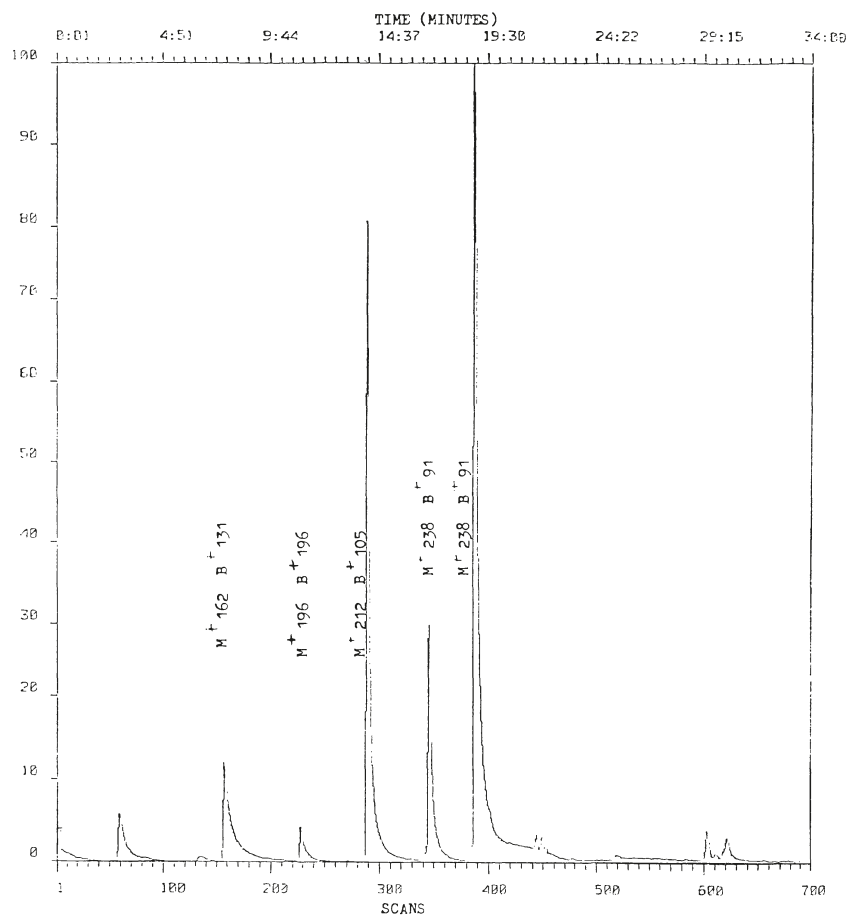
chromatography and infra-red analyses the gum–resins galbanum and olibanum as well as beeswax and asphaltum. The resin galbanum was detected by identification of the coumarin component, umbelliferone, as well as the sugars arabinose and galactose, in the hydrolysed aqueous extract. Worthy of note was the failure to detect colophony, mastic resin, sandarac and myrrh as well as labdanum, bdellium and storax, by gas-chromatography and thin-layer chromatography [48]. Unfortunately the report is brief with little experimental detail. Nevertheless it is clear that this material can be very variable and no doubt different components were used according to availability.

Fig.4 is an example of the chromatogram afforded by a sample labelled powdered mummy. The substance had given positive furfural and ninhydrin tests, indicating the presence of polysaccharide and proteinaceous substances. It was dark brown in colour and appeared to consist of a large amount of finely-divided material, mixed with somewhat coarser particles and textile fibres. There was noted a certain analytical variability between these coarser particles and the finer granules, though more in a quantitative rather than qualitative sense. Certainly the chromatogram revealed the presence of non-drying fats, seemingly animal tallows rather than seed oils. This was further supported by a specific mass scan for mass m/z 386, the molecular ion of cholesterol. Moderate amounts of cholesterol and its oxidation products would only be expected in animal tallows or egg fats. No evidence was found for the inclusion of beeswax since there was an absence of higher esters and hydrocarbons. Furthermore there was no suggestion of the use of asphaltum or bitumen. Traces of dehydroabietic acid and its oxidation product did appear to indicate a conifer resin input to the mixture, possibly residues of cedar resin.

Geologically modified organic material

Bitumen and asphaltum

Such materials seem to have found application as pigments for oil painting, but nevertheless are known for the considerable problems that they cause in the drying and continuity of the oil medium film. Asphaltum was said to have been greatly favoured by the Flemish Masters [49]. De Mayerne states that asphaltum was not ground, but was pulverized and dissolved, mixed with a drying oil prepared with litharge by heating. References to the use of asphaltum with copaiba, Venice turpentine or *olio d'Abezzo* (balsam of *Abies alba*) are not uncommon and an example appears in *A Compendium of Colours* [50]. The author made no comment concerning the poor drying, flowing and cracking of this mixture! Moreover, speaking of brown colours for shadows on flesh tones, he maintains that the asphaltum chosen should be very pure, very black and friable. Williams [51] pays great attention to the manufacture of a modified asphaltum known as 'Antwerp brown'. He remarks that it is, '[. . .] not to be had in the shops at present', and goes on to say that it is of great value by virtue of its depth of colour and tone. He speaks of its 'great body' and says that it will undoubtedly stand well. It

Figure 4 Saponified and methylated sample of powdered Egyptian mummy pigment. Note the presence of stearic and palmitic-rich glycerides, coupled with traces of cholesterol. This must suggest the use of animal fats in the original composition. There is also evidence for the presence of conifer resin (dehydroabietic acid), whilst the appearance of moronic acid in the sample is consistent with mastic resin.

Analytical conditions: similar to Fig. 1, but temperature programmed from 150°C by 7°C per minute to 350°C.
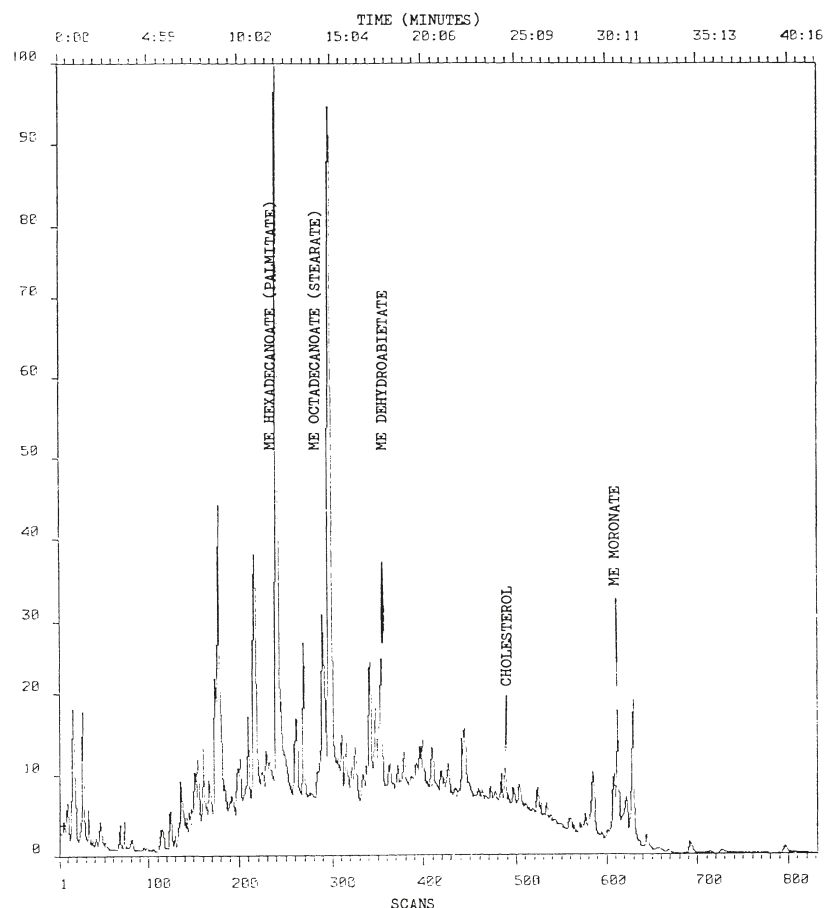
was prepared by putting good asphaltum into an iron ladle and placing it over a slow fire, where it was to be boiled until it would 'boil no more' and went into a cinder. Thereupon it was cooled and sugar of lead was mixed in, the whole being then ground into the strongest drying oil. Eastlake comments that this treatment was probably sufficient to prevent the cold flow of the asphaltum and perhaps rendered it less likely to crack or crocodile. Moreover Eastlake alludes to the practice of the French painters of the school of David who were said to have added wax to bitumen when dissolved in the 'usual' way.

Williams relates the practice of enriching browns with a yellow glazing pigment over the surface. He makes an objection to the use of 'brown pink' and goes on to suggest that a better colour can be made from the application of Antwerp brown and yellow lake [51,52].

Bitumen and asphaltum represent the waxy residues from crude petroleum which will, in part, distil between 300 and 540°C. Their chemistry is fairly variable and certainly very complex. Aliphatic hydrocarbons, alicyclics, polycyclic aromatic hydrocarbons (PAHs) and nitrogen bases have all been identified in a range of samples. The terms asphalt and bitumen are used rather loosely and are not clearly distinguishable, being derived from the Greek and Roman names for the same material. Nowadays the term bitumen tends to be used for the more lipid-like components (maltenes) occurring with little mineral matter intermixed. The term bitumen is typically reserved not only for the natural residues of low volatility left from petroleum, but also that distilled artificially. Asphalts occur as outcrops remaining from original seepages of crude petroleum via rock fissures through to the surface or exposed as a result of erosion and weathering. Bitumens and asphalts generally occur where there are areas of volcanic activity or hot springs. Examples are the bitumen pits of Ur, the bitumen springs of Zakinthos and the asphalt lakes of Trinidad. In the context of painting, it is likely that the bitumens, true asphalts (< 10% associated mineral matter) and rock asphalts (> 10% mineral) are all encompassed by the general term 'asphaltum'. The higher melting point, barely fusible asphaltites such as Gilsonite and glance pitch were probably not suitable for use until modern grinding techniques enabled very small particle sizes and consequential ease of suspension in a medium. These materials are very complex mixtures of aliphatic hydrocarbons, alicyclics, PAHs, carbon polymers, heterocyclics and other nitrogen bases. The typical bituminous content of crude petroleum, that is the black, waxy lipid-rich residues accounts for about 2% of the original and of this the triterpane content amounts to a few percent. It must be said that successful characterization of asphaltum in actual paint samples requires very sensitive techniques of high resolving power. GC–MS appears reasonably well-suited for this purpose.

These materials represent the chemical fossils of organic components originally present in cell membranes of living marine plankton and more importantly, bacterial systems. In addition there may also have been varying inputs of organic debris from terrestrial plant sources. In contrast to coal, petroleum originates predominantly from sediments accumulating at the bottom of the sea or lakes. As the debris accumulated and these layers sank deeper and deeper under newly deposited matter, so the pressure increased

and with it the temperature of the stratum. In this environment, devoid of further oxygen input, it is hardly remarkable that functional groups (that is, oxygenated groups) were eliminated from the various molecular species, hydrogen transfer from one molecule to another (disproportionation) took place, as well as progressive cleavage of methylene units from vulnerable side-chains. In part these processes were assisted by catalytic surfaces supplied by embedded mineral grains. In those sediments where there was a reasonable input of detritus from green marine algae and plankton, chlorophyll is found, which is a heterocyclic-based porphyrin nucleus with isoprenoid chains attached. As a result of the metamorphic processing within the compressed stratum, we end up with aromatic heterocyclic macromolecules derived from porphyrins and sheets of polymers based on fused aromatic rings, as well as isoprenoid side-chain fragments, such as pristane and phytane.

In essence the chemistry of asphaltum is that of the less volatile crude petroleum residues. The process of formation of these materials takes place over millions of years and to some extent they still exhibit the chemical skeleta of the original biological remains. Prominent biological markers include hydrogenated and aromatized terpenoid skeleta, pristane, phytane, cyclic mono- and diterpanes. A range of steranes and triterpanes have been identified, derived from phytosterols and bacterial triterpenoids. Cholestanes, pregnanes and ergostanes dominate the overall catalogue of steranes. Sterenes and stanols are of significance in recent sediments that have only partly undergone fossilization.

A sample of aged bitumen from the Zakinthos bitumen springs illustrates quite well the composition of a typical asphaltum. Fig.5 shows the total ion chromatogram for the benzene extract of a sample of the bitumen. The steranes can be detected by a mass scan of m/z 217, being the base peak for the cholestane series and m/z 231, base peak for the 4α –methylcholestanes. Fig.6 is a mass scan for m/z 191, which reveals the preponderance of the hopane class of triterpanes. This range of hopanes must surely suggest a major contribution of the extended hopanoids derived from bacteriohopane to the original sediments. Bacteriohopanoids are unusual in nature and are restricted to procaryotic organisms — bacteria. The presence of a range of hopane homologues is an excellent indication of the asphaltic nature of a sample. They are not found in the tar and pitch of wood and resin.

Fig.7 shows the total ion chromatogram for the benzene extract of a sample of black bituminous-looking paint that had shown signs of cold-flow.

References [53–60] give a selection of papers on the chemistry and fingerprinting of bitumens and asphalts.

Pyrobitumens

Coal: When used as a pigment it was called *sme-kool* or forge-coal by Van Mander and seems to have been used in watercolour as well as oil medium. It generally gives a somewhat brownish tint. De Mayerne states that shadows of flesh may be well-rendered by pit-coal, which should not be burnt. Several other writers of those times make mention of it, including a reference in the Norgate manuscript, which specifies that *small cole* or *charcole* (carbonized vine stalks) is a blue-black, whilst *sea cole* makes a red-black. Early Flemish illuminators such as Gerard of Bruges

Figure 5 Aged film of bitumen from Zakinthos. The benzene-soluble fraction was examined without methylation. The chromatogram represents a total ion plot and illustrates the sterane/triterpane region. The homologous series of hopanes peak at 17α(H)-norhopane. The labels moretane, oleanane and hopanes refer to the skeletal types and not the parent compounds.
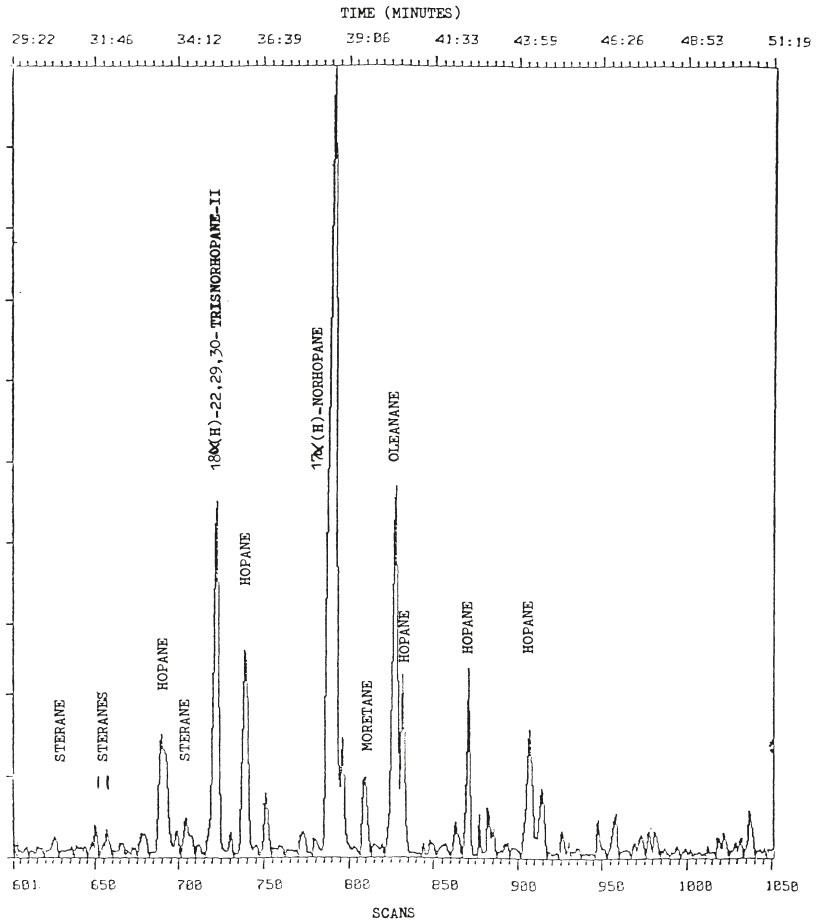
Figure 6 'Hopanogram' or specific ion chromatogram for *m/z* 191, representing the most intense fragment in the mass spectrum (base peak) for the hopanes. This clearly shows the preponderance of this class of triterpane in this type of sample.

Analytical condions (Figs. 5 and 6): Grob splitless injection onto 12 metre SE30-equivalent bonded phase (0.3 mm. inner diameter); temperature programmed from 90°C by 3°C per minute to 300°C; 70eV electron impact mode; 1 second per decade scan rate.
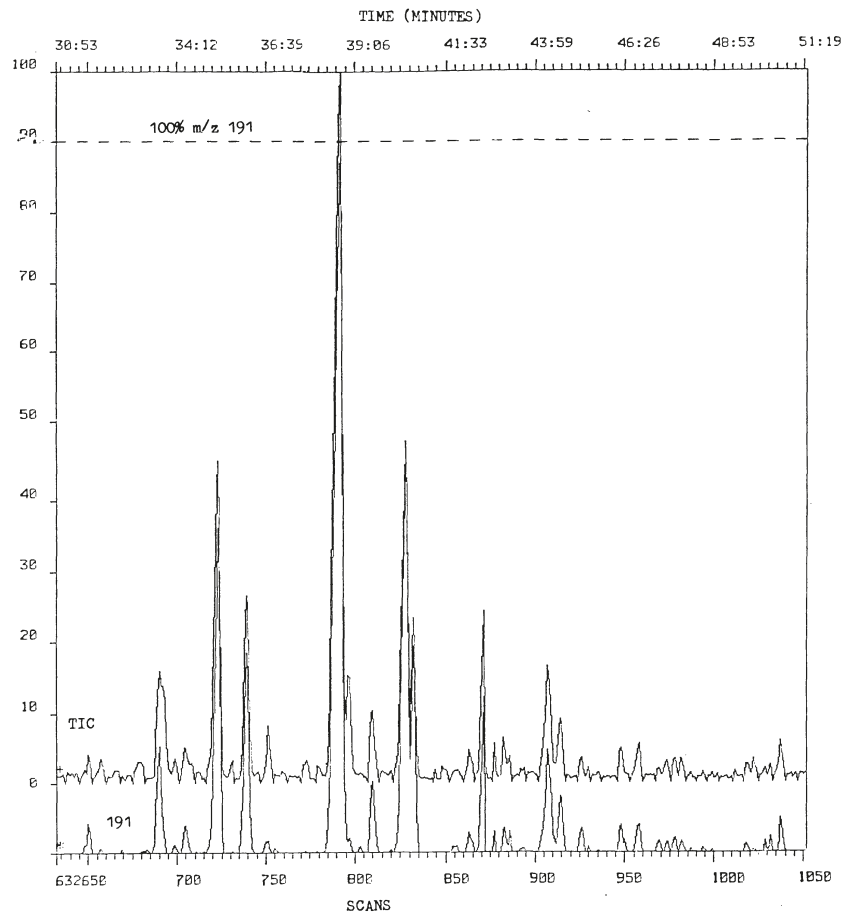
were in the habit of using a warm black pigment prepared from common coal (*schmiederkohlenschwartz*).

Coals have a much lower ratio for hydrogen to carbon content than do asphaltic and bituminous materials. This is a direct result of the nature of the input material prior to fossilization. It would seem to be mainly lignin from terrestrial woody plants, which is converted into carbon poly-cyclic polymer sheets.

Lignites and peats: Van Dyke brown, variously anglicized to Vandycke and Vandyck brown was undoubtedly known prior to the seventeenth century. It was given that name owing to the popularity which it attained during that period. It was also known as Cologne earth and is, in essence, an organic brown pigment whose source would appear to be lignitic or peat deposits. Hence its name Cologne earth for it was indeed dug up from the earth. Nevertheless it is certainly not a mineral pigment, but is mainly organic. The latter name was generally used in England until more recent times. Hilliard speaks of it as being suited to the shading of blacks and browns and Marshall Smith stipulates that it is a pigment that should only be used with drying oil. Towards the end of the eighteenth century a distinction was made between Cologne earth and Cassel earth. Apparently Vandycke brown had become synonymous with the latter; it is most likely that these represent varying samples of lignite or peat. De Mayerne refers to *Colniche Erden*. As might be expected it retards the drying of an oil, even when mixed with a good lead drier.

## Artificial products formed by pyrolysis

Resin, softwood tars and pitches; smoke condensates

Tars: These can be classified as low temperature or high temperature tars. We are solely concerned with low temperature tars. They are essentially pyrolysis products resulting from the carbonization of typically wood and, in the later eighteenth and nineteenth centuries, coal, peat and lignite by dry distillation up to about 700°C.

There are two types of wood tar that have been available in the past, either softwood (a resinous wood tar) from conifer trees such as pine and spruce, or hardwood tars, mainly from oak and beech. Distillation of hardwood yields a condensate that consists of about 7% tar, which is reported to contain a complex mixture of acids, esters, alcohols, phenols and their methyl ethers and waxes. Beechwood is probably the only wood tar subjected to a straight distillation and the heavy oil fraction (bp 180–240°C) is nowadays important for the beechwood creosote produced from it. There are few references to recipes involving the use of these organic materials in European easel-painting technique. And yet such components have been available and used as adhesives, protective coatings and medicinal preparations from the earliest times. When mixed with oil, one is able to produce a variety of orange through dark brown glaze-paints. Without doubt they would serve eminently well as glazing layers required to impart warmth to shadows and skin-tones and prove invaluable in the modelling of folds in

Figure 7 Black paint from van Dyck's *Portrait of a Man*, Royal Collection. The paint showed evidence of cold-flow. The sample was exhaustively extracted with hot benzene and examined by GC–MS without further treatment. The upper trace is the total ion chromatogram, whilst set below is the corresponding hopanogram (*m/z* 191).

Analytical conditions: as for Fig. 1, but at 70 eV and temperature programmed from 120°C to 320°C at 7°C per minute.
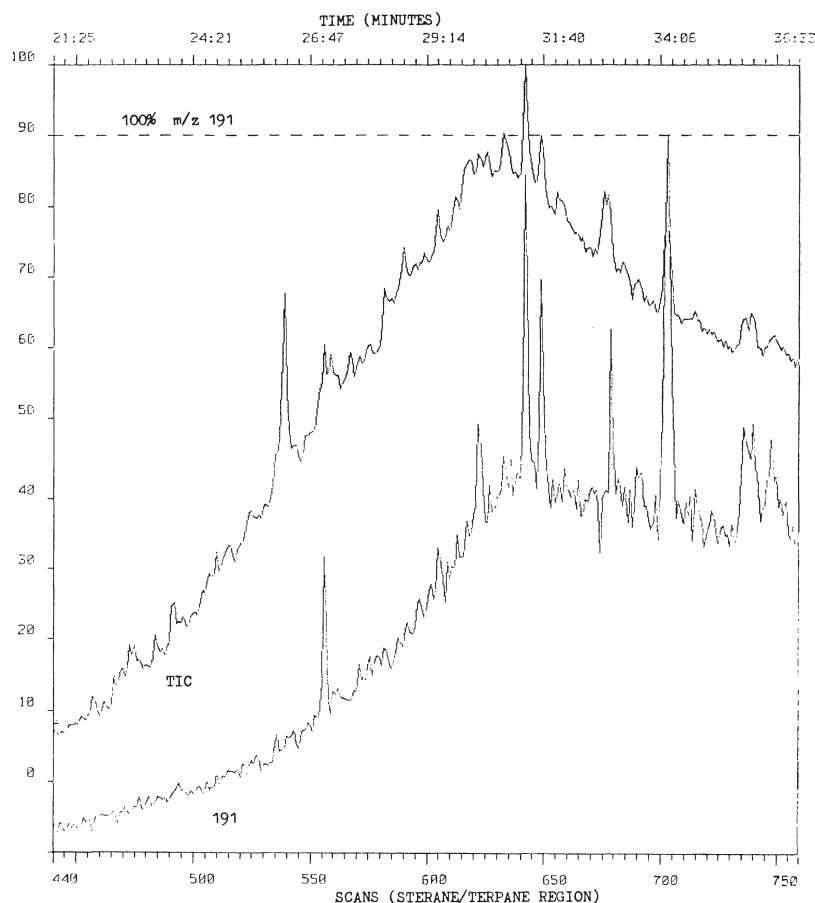
drapery. A non-terpenoid gum-resin, gamboge (from *Garcinia* sp.), when burnt, was recommended as a good glazing brown similar in colour to asphaltum [61]. It must be said that such materials present in paint media have a decidedly inhibiting effect where drying is concerned. Moreover they encourage long-term paint film defects much as with the case of asphaltum. No doubt wood and resin tars and pitches were used as more readily available and cheaper substitutes for bitumen and asphaltum since they have featured in pharmacopoeia from the earliest times. Watin [62] records that asphaltum was frequently adulterated with pitch and that asphaltum purchased in Holland was generally the residuum from distillation of oil of amber. Certainly the drying problems are no worse and possibly slightly less than those associated with asphaltum; moreover to some extent they could be satisfactorily offset by the inclusion of lead driers. It is far from clear why it should be that a resin tar should cause the same dried film defects as a softwood tar, both being much the same as those associated with asphaltum. In the case of a softwood pitch, one is well able to see that the production of phenolic fragments inhibits the drying of the oil component in the medium. This effectively means that assuming the tar component is evenly distributed throughout the paint film, the phenolics in the top layers will be used up first and the cross-linking of the glycerides will proceed first. The lower levels of the film, where oxygen availability is somewhat lower, will be protected against radical chain formation for a longer period. As a result the surface skin will dry and contract during hardening pulling the lower, softer layers into the characteristic 'islands' — that is, crocodiling and wrinkling will occur.

Rosin tar and softwood tar: These substances have been widely available from the Iron Age period throughout Europe and are by-products of charcoal production. There are a few references to their use in recipes, but the solidified and ground products must have been commonly confused with or used as adulterants for asphaltum. Thus it is hardly surprising that there are few specific references to these materials. Nevertheless Armenini, writing in the sixteenth century, mentions the smoke of Greek pitch (that is, pine resin tar) being incorporated with verdigris (as a drier) previously ground with oil [63]. He was widely plagiarized by writers, particularly in the seventeenth century and sections of his work were republished. Figs.8 and 9 show chromatograms of a softwood tar and a sample of thick glaze paint from *The Incredulity of S. Thomas* by Cima da Conegliano (No.816). See also p.17.

Softwood tars and resin tars are chemically somewhat similar. Both are produced by destructive distillation — of resinous conifer woods (pine and spruce, typically) in the former case and rosin in the latter. Their chemistry is dominated by dehydroabietic acid with lesser amounts of decarboxylated, demethylated and dehydrogenated pyrolytic products formed from this. These include compounds such as 18–norabietatriene, 19–norabietatriene, retene and 1,2,3,4–tetrahydroretene.

The chemistry of some wood tars and pitches has been reported [64,65].

*Bistre:* This was a rich transparent brown pigment which seems to have been prepared from wood soot, beechwood being preferred. After collection of the soot, it was treated with hot or boiling water and when the particles had settled out, the supernatant liquors were decanted and the sediment taken to dryness. It was called *fuligo* or *fuligino* by medieval writers and would appear to have been a principal brown pigment amongst the few available to the Italian painters. Reference was made to bistre under the name *caligo* in the manuscript of Jehan le Begue. As far as citations of its use in English sources are concerned, there would appear to be little prior to the eighteenth century. However, during this century it is mentioned fairly frequently. Bistre seems to have been reserved for watercolour medium, being said to provide a superior colour in that medium. However there is one minor drawback to its use in that it has a slightly resinous quality and so tends to prove difficult to work and less amenable to mixing with other colours. To offset this, Spanish liquorice (see p.59) extract was recommended as an additive. The liquorice extract not only masked the hydrophobic characteristics of the bistre but also provided additional (but vulnerable) pigmentation. A bistre produced by the artists' colourman Ackermann at the end of the eighteenth century was renowned for its improved working and mixing qualities and may be an example of the commercial incorporation of liquorice extract. Nevertheless, during the course of the nineteenth century bistre seems to have been largely displaced by sepia brown. It is somewhat curious that bistre was not reported to be used in oil medium, for in many ways it is more suited to application in this binder in view of its slight lipophilic tendencies. Although there may well be a certain slowness in drying of the oil, unless metal driers are employed, it should show a lower tendency to crocodiling than bituminous and asphaltic pigments.

Fig.10 shows a typical chromatogram of the neutral components from beechwood bistre. Note the presence of 5–membered alicyclic rings such as acenaphthene ($C_{12}H_{10}$, $M^+ = 154$), fluorene ($C_{13}H_{10}$, $M^+ = 166$) as well as fluoranthene ($C_{16}H_{10}$, $M^+ = 202$) found in all pyrolysates of organic materials whose molecules are large enough. Once these systems are formed, they do not easily revert to *peri*-condensed aromatic hydrocarbons. Polynuclear aromatic hydrocarbons (PAHs) are not particularly common in petroleum and its residues, but are significant components of high temperature pyrolysis distillates such as smokes and tars as well as their pitches or residues. Curiously PAHs such as benzopyrene, pyrene, perylene, benzoperylene and coronene, being *peri*-condensed compounds are of much greater reactivity than angularly condensed forms. As a result tars and similar materials with significant amounts of these must certainly have been subjected to quick cooling after formation for such components to have survived.

Charcoal black (or blue-black) and carbon blacks: Traditionally these were produced by a very slow carbonization process under anaerobic conditions, vine twigs being favoured as a source especially for use with oil paint. The 'Volpato Manuscript' from the last quarter of the seventeenth century suggests the use of plum tree and willow wood, packed tightly in an iron tube and the ends being stopped up with ashes. The tube was heated to red heat until no more smoke was produced and then cooled in water. Other sources invoke the use of oak wood, peach stones,

Figure 8 Softwood tar, methylated ether extract. The main component is the resin acid ester, methyl dehydroabietate. Some methyl pimarate remains. The presence of decarboxylated and partially aromatized diterpenoids confirms the pyrolytic genesis of this material.

Analytical conditions: as for Fig. 6, except that the column was temperature programmed from 120°C to 305°C at 5°C per minute.
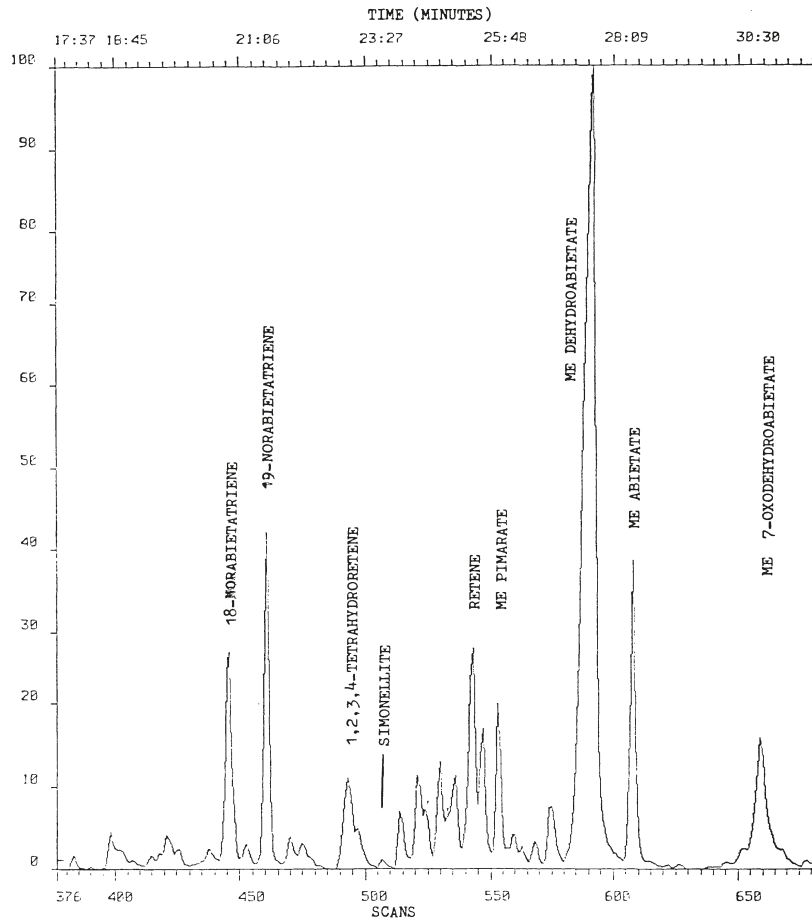

Figure 9 Thick orange-brown glaze over yellow paint, Apostle's cloak, Cima da Conegliano, *The Incredulity of S. Thomas* (No.816). The sample was exhaustively extracted with benzene and methylated before analysis. The chromatogram shows fatty acids from the drying oil present and methyl dehydroabietate, indicative of resin from a conifer source (probably pine). Traces of retene and norabietatrienes suggest that a softwood pitch has also been incorporated in the mixture.

Analytical conditions: As for Fig. 1.
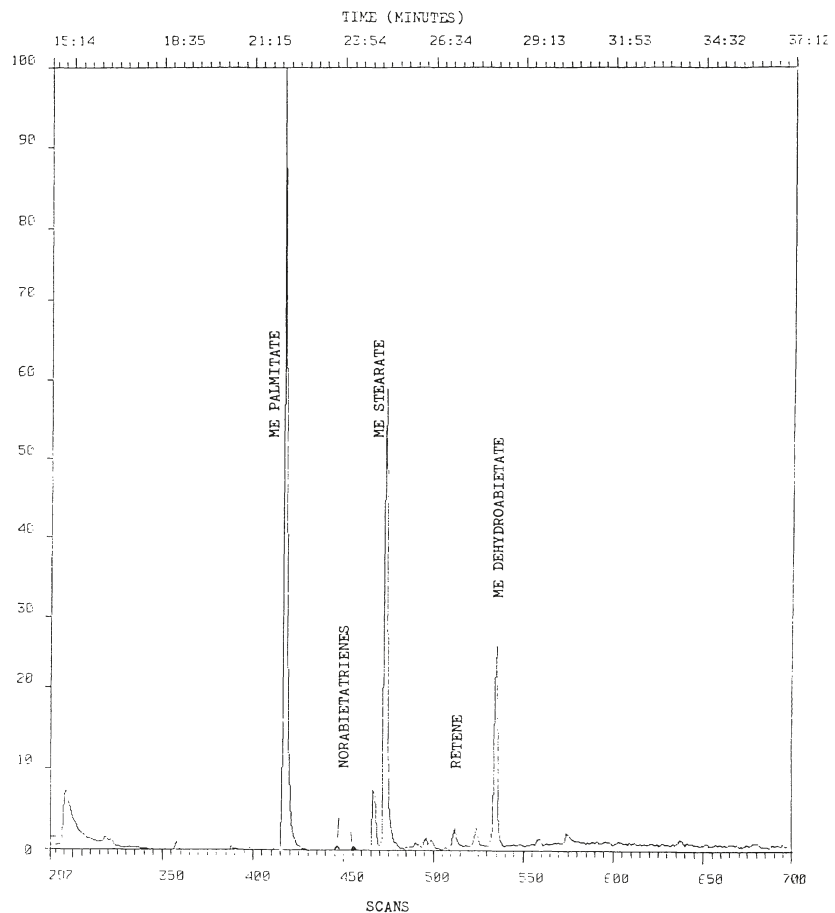
Figure 10 Benzene extract of aged beechwood bistre film, unmethylated. The total ion chromatogram depicted shows traces of polycyclic aromatic compounds such as fluoranthene, pyrene, acenaphthene, perylene and very small amounts of benzopyrenes and coronene (not shown). A major component at scan 483 seems to be a useful indicator and a tentative assignment of. structure is given. In addition the methylated material shows a series of higher fatty acids and other acidic components.

Analytical conditions: As for Fig. 1, but at 70 eV and temperature programmed from 150°C by 7°C per minute to 350°C.
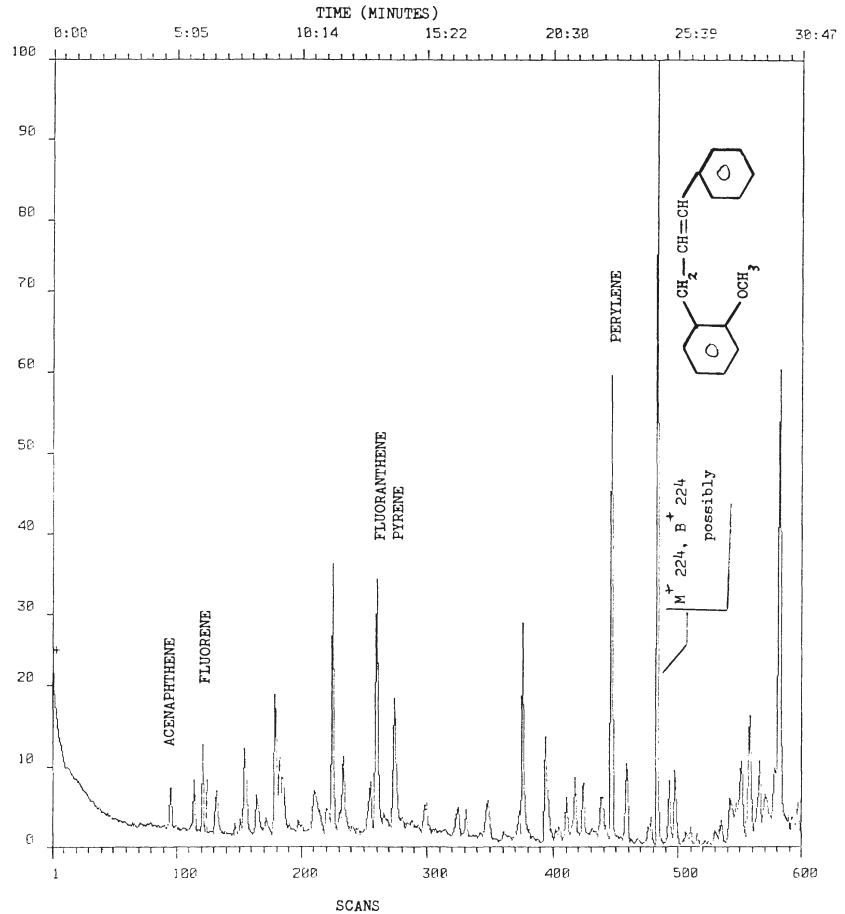
Figure 11 Sample of commercial lamp black pigment. The sample was exhaustively extracted with aliquots of superheated benzene and the concentrate injected directly onto the gas-chromatograph. The main components seem to be pyrene and perylene. There was some evidence for hydrocarbons under the chromatographic envelope.

Analytical conditions: As for Fig. 1.
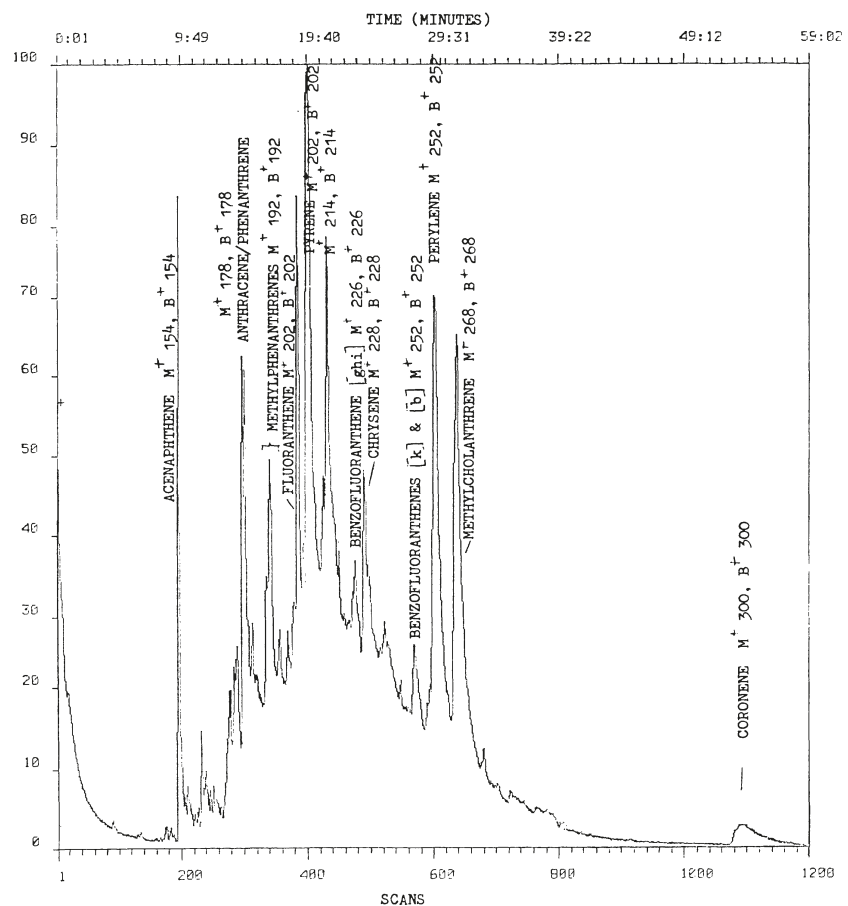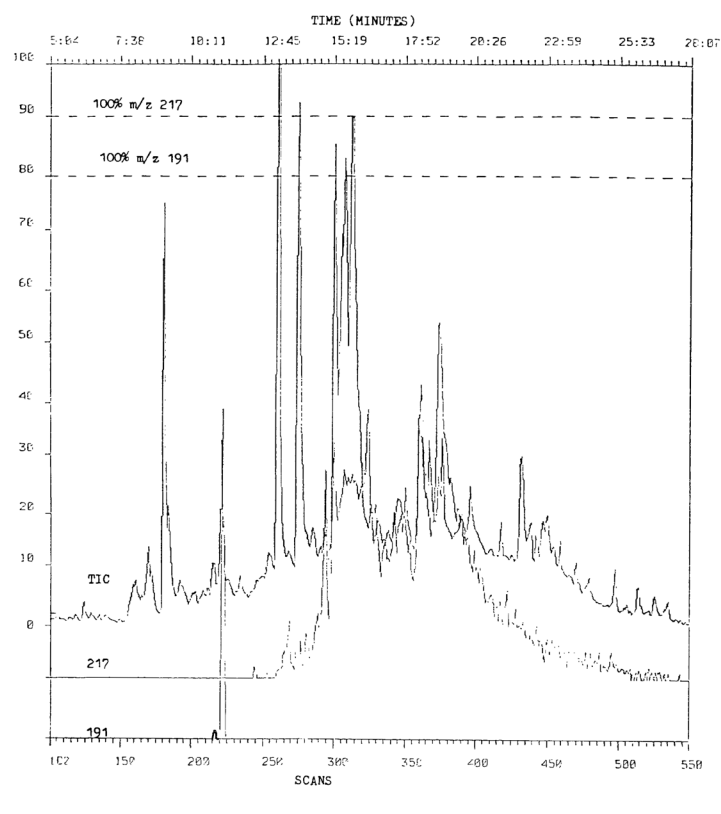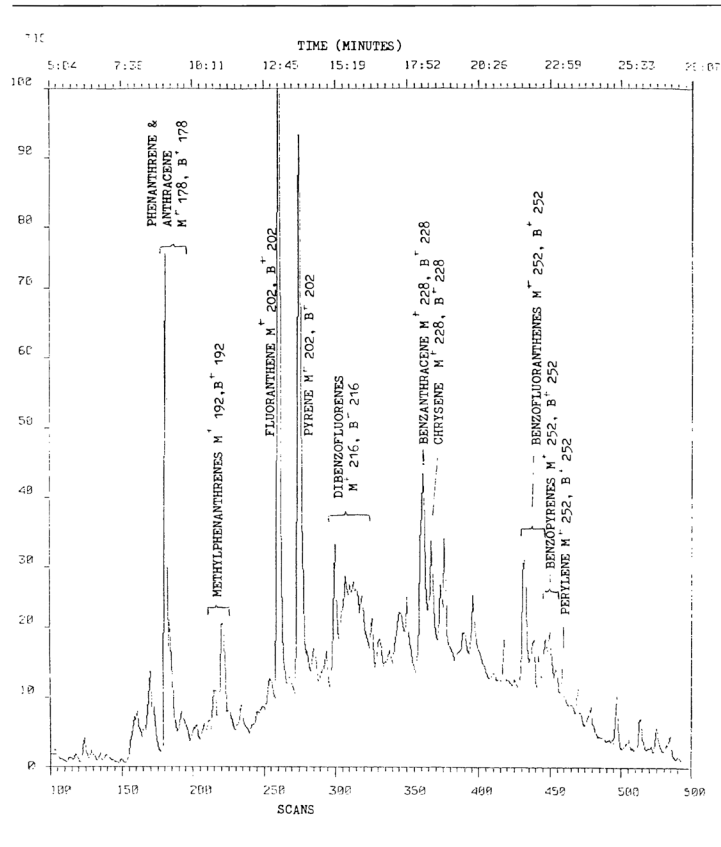
whilst Cennino Cennini mentions almond shells and even paper. Mrs Merrifield relates that this latter form of preparation was still employed in Italy during the nineteenth century. The charcoal seems to have been ground, best with water, and then if not mixed with other colours, was used in 'strong' oil, that is drying oil with driers. Strictly speaking, these materials cannot be classified as organic since they consist mainly of free, elemental carbon or carbon polymer. Indeed they are best identified by microscopical means. By this technique it is often possible to see remnants of carbonized cellular material resulting from the woody structure of the starting material. There is a useful information sheet for charcoal identification in archaeological specimens and paleobotanical studies [66]. Nevertheless trace amounts of degraded organic components do survive — notably where the earlier, less complete carbonization processes were employed. Under these conditions, this organic pyrolysis material can be strongly adsorbed to the active surface of the carbon. Generally the adsorbate consists of polynuclear aromatics in which 5-membered rings predominate with traces of hydrocarbons derived from waxy hydrocarbons. Fig.11 shows the total ion chromatogram of the soluble part of lamp black exhaustively extracted with boiling benzene aliquots. Traditionally prepared lamp blacks have somewhat larger particle size (typically twice) than furnace or channel blacks, but in addition it has been reported that the latter contain more highly oxidized PAH derivatives such as ketones and quinones, acids, anhydrides and nitro-compounds [67]. Examination of the chromatogram reveals the predominance of pyrene, together with fluoranthene, benzofluoranthene [j or k], perylene or benzo[a]pyrene and coronene. In the manuscript of Jehan le Begue [68] lamp black is given as fumus and was described as collected soot from candles or oil lamps. It would seem to have been preferred for use with drying oil to ivory black in that the latter slows down the drying of the oil to a greater extent and the corruption of the colour by common adulteration of it by charcoal black, thereby rendering it of a 'blue cast'.

Coal tar: This is another pigment that may have crept into the artists' palette during the eighteenth and nineteenth centuries. This material is produced by the destructive distillation of coal, usually in closed retorts under anaerobic conditions. It is a product that consists of a complex range of chemical components. Though liquid when freshly exposed to the air, it dries by loss of the more volatile

Figure 12a (left, top) Benzene solubles, unmethylated, of aged coal tar film; total ion chromatogram. Here the main components are polycyclic aromatic compounds of which fluoranthene, pyrene and phenanthrene/anthracene seem to be the major compounds.

Figure 12b (left, bottom) Combined hopanogram, m/z 217 mass chromatogram and total ion chromatogram. Only two peaks within the sterane/triterpane region exhibit a fragmentation pattern with a significant proportion of m/z 191. In fact these fragments occur under the methylphenanthrene envelopes and so merely represent an isotopic contribution from the molecular ion at m/z 192. Clearly hopanes are absent, unlike the case for asphaltic materials. The m/z 217 mass scan highlights those components likely to be cholestane-like steranes (base peaks typically at m/z 217).

Analytical conditions: as for Fig. 1, but 70 eV and temperature programmed from 150°C by 7°C per minute to 350°C.

components to form a substance that ranges from a semi-solid to a brittle pitch. In the latter state, it is indistinguishable as far as physical appearance and properties from some forms of asphaltum. Whether by design or accident, coal tar must often have been substituted for bitumen or asphaltum. Both suffer from the same paint defects and slow down the drying of oil media, the former more so than the latter for coal tar contains a far greater amount of phenolic fragments, which act as anti-oxidants and delay free radical formation and subsequent cross-linking in the drying oil. Fig.12a illustrates a chromatogram for a typical coal tar residue and represents the benzene soluble fraction, unmethylated. We can immediately see that the *peri*-polynuclear aromatic hydrocarbons (PAHs) are fairly major components. Only traces of the lower molecular weight substituted naphthalenes survive having been lost by diffusion and evaporation at the surface of the film. Since the *peri*-PAHs, pyrene and the benzopyrenes being good examples, are reactive at elevated temperatures, the chromatogram would suggest that the distillate was cooled fairly promptly for them to have survived in reasonable quantities. Furthermore, the presence of 5-membered aromatic ring components in reasonable strength confirms the pyrolytic genesis of the material, since these are relatively stable at high temperatures. Interspersed amongst the PAHs, one may see small amounts of hydrocarbons, characterized by their base peaks at m/z 57. Fig.12b shows a cross scan for cholestane-like steranes and hopane-like triterpanes. Though there are peaks representing a contribution from m/z 191, the main ones at scan 216 and 222 represent only the isotope peaks associated with two isomeric methylphenanthrenes of molecular weight 192. The esterified sample showed little in the way of acids, especially higher 'waxy' acids and so is unlikely to be confused with other pyrolysis products such as bistre.

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