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APPLICATION OF COMPOSITIONAL ANALYSIS TO THE STUDY OF MATERIALS AND OBJECTS OF ART AND ARCHAEOLOGY

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Archaeologists, art historians and art conservators are almost constantly concerned with the questions of where, when and by whom the objects within their care were made. Knowledge of the conditions under which the objects were found may not answer these questions, as the objects may have traveled extensively or have existed for some time before they arrived at sites where they were discovered. Stylistic considerations often can provide answers, but not infallibly, as styles were sometimes copied at locations and at times quite different from those for which they were most characteristic. Compositional analysis can often help provide answers to these questions because traditions in the use of particular materials have often persisted in and accordingly have been characteristic of particular regions, periods and even of particular workshops. For example, the deliberate alloying of copper with tin, arsenic, antimony, lead and/or zinc has varied greatly from region to region and from time to time.

Raw materials from a particular source, such as clay from a specific deposit, often contain distinctive, unique compositional patterns, particularly in the levels of trace impurities present within them. These identifying compositional patterns are often found to persist in objects made from these materials, as, for example, in pottery made from a particular clay. Hence the quantitative determination of many components within objects often has been used to infer the geographic origin of the object, or at least the origin of the materials out of which it was made.

Compositional analysis is often essential when one is attempting to infer how and of what materials an object was fabricated. It is also often required to gain an understanding of the nature and degree of deterioration or other alteration an object may have experienced since it was made. Compositional and structural analysis usually go hand in hand in such studies, and, in fact, the same measurements sometimes produce both compositional and structural information. For the purposes of this paper, any method of measurement that either qualitatively identifies the presence of particular chemical elements, compounds or phases within materials or objects and/or quantitatively determines the concentrations of these substances will be considered to be a method of compositional analysis. The identification or determination of minerals within rocks or materials formed from rocks is an example of compositional phase analysis.

Virtually every method of compositional analysis yet devised has or can be applied to the study of works of art or archaeological artifacts. The chemical microscope is probably the most ubiquitous analytical tool in museum laboratories. For the determination of elements emission spectroscopy, X-ray fluorescence, atomic absorption and neutron activation have been the techniques most often applied, although such methods

as spark mass spectrometry and Auger spectroscopy have been so employed. X-ray diffraction and thin-section petrography are most often used for identification of crystalline phases. Various forms of spectrophotometry and occasionally nuclear magnetic resonance and Mossbauer spectroscopy have been used for measurement of specific molecular substances. Infra-red spectrophotometry, chromatography and chromatography coupled with mass-spectrometry have most often been used for the analysis of organic materials. Space will not permit examples of the use of all such methods to be presented, but many of them will occur in the examples of application of analysis that follow. It is to be hoped that new methods of analysis will be suggested by the participants of this symposium.

Ancient glass will serve well to illustrate many of the archaeological points of interest to be inferred from analysis. It is a man-made material which was formulated quite differently in different regions and at different times. The earliest production of glass in any great quantity occurred in the middle of the second millennium B.C. principally in New Kingdom Egypt and in Mesopotamia. Surprisingly analysis has shown it to be a soda lime glass very similar in composition to the common window or bottle glass of today. It contained roughly fifteen percent sodium oxide, seven and one half percent calcium oxide and seventy percent silicon oxide with about two percent aluminum oxide, one to two percent magnesium oxide, one percent potassium oxide and a number minor and trace impurities [1]. The glass was largely formed into inlays and into "sand-core" vessels. These vessels were formed by laying heated, semi-fluid glass onto the surface of porous cores made of sandy clay and lime and then rolling them on rock slabs perhaps using paddles to smooth out and consolidate the glass. After formation the core was removed to leave the vessels hollow. Figure 1 shows an example of an early Egyptian sand core vessel.



Fig. 1 New Kingdom Egyptian Sand-core Vessel, 2nd M. B.C.

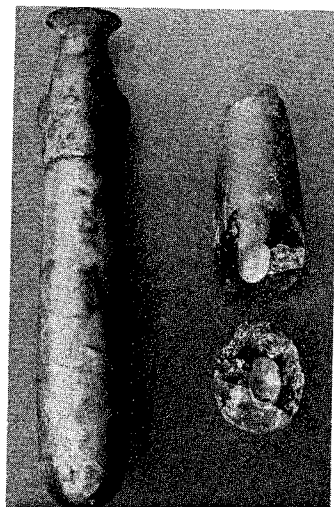


Fig. 2 Mediterranean Glass Vessels, 7th Century B.C.

A hiatus in social and technical development occurred following the New Kingdom period, during which time little or no glass seems to have been made. When glass manufacture resumed in the western mediterranean region during the first half of the First Millennium B.C. its formulation had distinctly changed [2]. Some examples of about 7th Century B.C. glass vessels from Italy and Cyprus are shown in Figure 2. The glass now tends to be colorless and clear rather than colored and opaque and has been formed by being cut from a solid block rather than being formed around a core. This new glass was still basically a soda lime glass but it now contained distinctly less potassium and magnesium than had the earlier glass. Glass of this composition continued to be made throughout the Roman Period, Figure 3. Figure 4 shows the distributions of sodium, magnesium, potassium and calcium oxides in several hundred specimens of ancient western glass that were analyzed at Brookhaven National Laboratory. The figure shows that they fall into two types, the ones shaded more darkly being richer in both potassium and magnesium. The overlapping distributions of sodium and calcium oxides for the two groups confirm that they were both soda lime glasses.



Fig. 3 Roman Glass Vessel Blown into a Mold, 1st C. A.D.

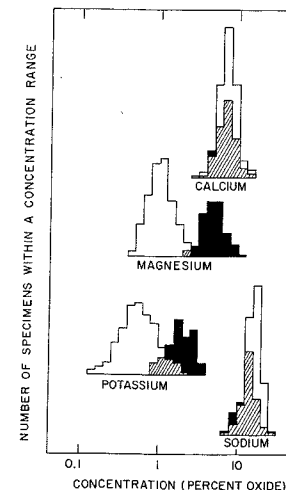


Fig. 4 Oxide Distributions in Western Ancient Glasses.

Since both potassium and magnesium are elements one associates with alkalis it would seem likely that the difference in the two glasses could be ascribed to two different types of alkalis being used in them. The glass composition with low potassium and magnesium is consistent with one in which natron, the naturally occurring sodium carbonate found at the Wadi Natrun in the Egyptian western desert, would have been used. Ancient glass factories have been found in the Wadi Natrun in which natron must surely have been used. It is also well known that natron was a major item of commerce in the ancient world. The glass composition with high potassium and magnesium is consistent with one in which

sodium carbonate obtained by evaporating Nile river water was used. In his *Natural History* Pliny [3] states that a form of natron was produced through the evaporation of Nile river water. It should be noted, however, that other types of alkalis, particularly the ashes of certain desert or marine plants, could also have produced glass of the two compositions encountered.

In the middle of the 9th Century A.D. Islamic soda lime glass, which, similar to Roman glass, had been of the low potassium, low magnesium composition returned to the high potassium and magnesium composition of 2nd Millennium B.C. glass. Also glasses containing as much as seventy percent lead oxide began to be used in Islamic areas [2].

Contrasting greatly with this early western soda lime glass is the early Chinese lead-barium glass [4]. The earliest major use of glass in China occurred at about the middle of the First Millennium B.C. during the Eastern Zhou Dynasty. This glass contained roughly 45 percent lead oxide, 13 percent barium oxide, 35 percent silicon oxide with a few percent sodium oxide and other more minor constituents. Clearly the first development of glass in China was independent of the glass manufacturing tradition that existed in the West. Interestingly enough, however, during the Han Dynasty, which coincides in time with the establishment of the Roman Empire and the first major development of trade between China and the West, the formulation of Chinese glass changes to a soda lime composition virtually identical to that of Roman glass. It would seem likely that in this instance China adopted a western technical development. More often, of course, the West imported technical developments from China.

Starting in about the 10th Century the formulation of glass in northwestern Europe underwent a significant change in which potassium replaced sodium as the predominant alkali. In these glasses, such as the ones one encounters in medieval cathedral windows, the potassium oxide concentrations are an order of magnitude greater than the sodium oxide concentrations. Some three percent phosphorous oxide and one percent manganese oxide are also present in these glasses which has lead people to infer that wood ashes, particularly beechwood ashes, was the source of alkali used in them [5].

Thus compositional analysis has shown that many changes have occurred in the choice of the raw materials used in the manufacture of glass, and in some instances it is possible to infer what these raw materials might have been. These occurrences of the different glass formulations have a definite chronological sequence so the observance of them in glass objects can provide a degree of rough dating.

Considerable interest has been taken in the colorants, decolorants and opacifying agents that have been used in glass. In one instance it has been possible to trace through analysis the exact source of a colorant. Some years ago I observed that comparison between the compositions of cobalt blue New Kingdom Egyptian glasses and those of corresponding colorless glasses showed that not only the cobalt concentration was enhanced in the colored glasses but the concentrations of magnesium, aluminum, manganese, iron, nickel

and zinc were as well [6]. In addition, enhancement to the same levels for all seven elements was found in Mycenaean cobalt blue glass of the same period, but not in Mesopotamian cobalt blue glasses. Clearly cobalt from the same source must have been used in the Egyptian and Mycenaean glasses. Recently Kaczmarczyk [7] has reported finding the probable source of the cobalt in that he discovered a pink alum at the Dakhla Oasis in Egypt's Western Desert in which the relative concentrations of the seven elements closely matched the pattern of concentration enhancement observed in the New Kingdom and Mycenaean glasses.

Exchange of objects over wide geographic areas, through commerce and other means, has been established through determination of coinciding compositional patterns within stylistically similar objects. An example of this is black glazed Greek pottery of the Classical and Hellenistic periods. A sizable number of pottery vessels of this type excavated at such widely separated locations as the Athens Agora, some Greek colony sites in Southern France, Tell el Hesi in Israel and Idalion and Larnaca on Cyprus have been found to have such closely matching concentrations of fifteen elements as to lead one to believe that they must have come from the same source [8]. Figures 5 and 6 compare standard deviation ranges for these fifteen components in the matching pottery from the four regions. In the figures the diamonds indicate the standard deviation ranges for specimens from Athens, France, Israel and Cyprus in order from left to right for each component. Since the specimens from Athens included test firing wasters from pottery workshops in the Agora we can be sure that pottery of this type and composition was made there. Therefore, it is logical to conclude that Athens was indeed the source of this matching pottery. To this day clay of this composition has not been located, and indeed the ancient clay source may well have been exhausted. Without the original clay it would be nearly impossible for a modern forger to duplicate the multicomponent composition of this classic pottery.

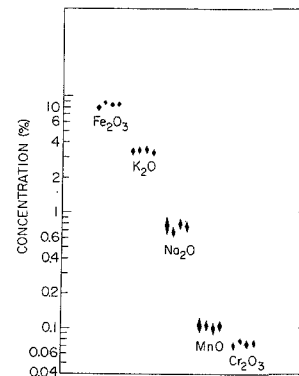


Fig. 5 Major and Minor Oxides in Classical Attic Pottery

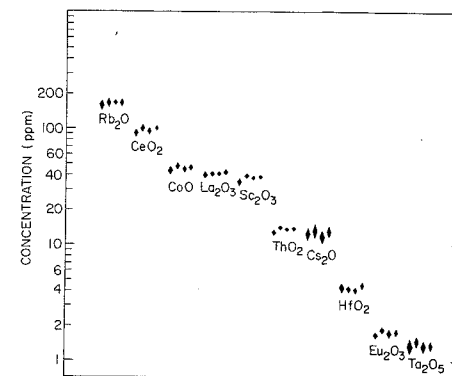


Fig. 6 Trace Components in Classical Attic Pottery

The determination of the relative concentrations of stable isotopes has been used extensively for characterizing and for inferring provenances of archaeological artifacts and works of art. The stable isotopes of carbon, oxygen, sulfur and strontium have all been used in the study of limestones, marbles and other rocks, and the four stable isotopes of lead have been used particularly in the study of metal alloys, and lead containing glasses and glazes. An example of such research is provided by the analysis of more than 300 specimens of early Chinese ritual bronze vessels from the Arthur M. Sackler Collections [9]. The specimens divided, roughly equally, into groups attributed to the Shang Dynasty (1523-1027 B.C.), to the Western Zhou Dynasty (1027-770 B.C.) and to the Eastern Zhou Dynasty (770-256 B.C.). The lead isotope ratios for these specimens span an unusually wide range in magnitude and group into clusters that show pronounced correlation with the stylistic attributions of the vessels. Most of these compositional clusters can be seen in Figure 7, which is a multivariate plot derived from the stable lead isotope ratios of $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$. Specifically it is a plot of standardized coordinates for the specimens in the principle component vector directions that account for the maximum variance among the specimens for these three ratios.

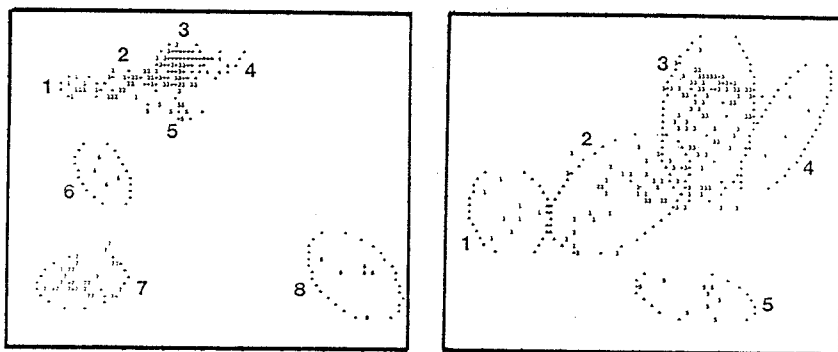


Fig. 7 Complete Plot Detail of Plot (Upper Left). Scatter Plot of Shang and Zhou Dynasty Ritual Bronze Vessels, Standardized Coordinates along the First and Second Principle Component Vectors for the Stable Lead Isotope Ratios $^{208}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$.

The widely separate group clusters 6, 7 and 8 are composed of only Shang Dynasty and relatively early Western Zhou specimens. Group 8 contains only Shang Dynasty vessels of relatively early date, 13-12 Century B.C. Moreover they are all of styles that have been encountered at the Shang capital Anyang. Group 7 is 92 percent composed of Shang Dynasty vessels but includes three vessels attributed to early Western Zhou. All of these vessels, including the early Western Zhou ones, are of styles related to Anyang. Group 6 is now considered to be early to middle Western Zhou.

The five relatively tightly clustered groups, whose resolution is shown in Figure 7B primarily contain Zhou Dynasty specimens, including only late Shang vessels. Group 1 contains one vessel considered to be borderline in date between Shang and Western Zhou with the remainder being Western Zhou. The largest group, Group 3, starts late in the Shang Dynasty, continues through the Western Zhou and terminates during the first half of the Eastern Zhou Dynasty. Stylistically it is a very diverse group relating to objects found in widely separated geographic areas. Groups 2, 4 and 5 contain no Shang Dynasty specimens and are composed, about equally, of Western and Eastern Zhou specimens.

These same ritual vessels were analyzed for trace elemental components by means of neutron activation analysis. These data also showed significant clustering but with less detail than the lead isotope ratio data. There was a good degree of correlation between the isotope ratio groups and compositional groups, however.

The stable isotopes of carbon, oxygen and nitrogen have been used for characterizing organic materials and a great deal of research has gone into establishing the relationship between $^{13}\text{C}/^{12}\text{C}$ and $^{15}\text{N}/^{14}\text{N}$ ratios in bone residues and the nature of human diets in antiquity [10]. Basic to these studies is the observation that during the creation of carbohydrate foodstuffs within plants through photosynthesis significant fractionation occurs among the light elements, and the degree of isotopic fractionation differs in different types of plants. Indeed the mechanism of photosynthesis itself can be quite different in different types of plants. It has been established that in most temperate zone plants carbon dioxide is first converted to a phosphoglycerate that has three carbon atoms. This is called the C_3 photosynthetic pathway. In certain other plants, notably sugarcane and maize, carbon dioxide is first converted to a dicarboxylic acid that has four carbon atoms, i.e., the C_4 photosynthetic pathway. The ratio of ^{13}C to ^{12}C is significantly greater in C_4 plants than it is in C_3 plants and this difference persists in the bodies of animals that feed upon these plants despite the fact that some additional fractionation occurs upon metabolism of the plant tissue. It has been observed, for example, through analysis of bones from datable burials that up until about 1000 A. D. the Indians of the North American woodlands, who were then primarily hunters and gatherers, had a $^{13}\text{C}/^{12}\text{C}$ ratio consistent with a diet derived from C_3 plants. Starting at approximately this time a steep rise is observed in the $^{13}\text{C}/^{12}\text{C}$ ratios in skeletal remains which would be consistent with the introduction of C_4 foods into the diet. This change has been interpreted as indicating the introduction of maize into the diet of these Indians, the corn being introduced from more southern regions.

The carbon dioxide dissolved in sea water has a significantly higher $^{13}\text{C}/^{12}\text{C}$ ratio than does carbon dioxide in air and as a result of this plant and animal foodstuffs from the oceans have nearly as high a carbon isotopic ratio and do C_4 plants. This difference has permitted the estimation of relative intake of marine and terrestrial foods in seashore regions in which C_3 plants are predominate.

The $^{15}\text{N}/^{14}\text{N}$ ratios in legumes, in non-leguminous C_3 plants and in C_4 plants have been found to be significantly different to serve as indicators of the relative amounts of these foods in diets. Some similar inference has been drawn from strontium isotopes but it has been contended that these isotopes are too subject to diagenetic change within buried bone to serve as reliable indicators of diet.

A major application of compositional analysis in museum laboratories is the study of conditions of deterioration within objects in order to understand the causes of the deterioration encountered and to suggest appropriate methods for its treatment. A study by Erhardt and Firnhaber [11] of oils found present in Hawaiian tapa cloth provides a good example of such research. Tapa cloth is a non-woven felted material made from the inner bark of some plants, notably that of the paper mulberry. It has been used in Asia, Africa and Central and South America, but is particularly associated with Polynesia. The cloth is sometimes oiled to improve its color and to make it waterproof and more flexible. However the oiled cloth eventually tends to become stiff and fragile. The study was to identify the oils used on a selection of Hawaiian tapas and to infer from this knowledge the reasons for the eventual deterioration.

Since there was good reason to believe that natural plant or animal oils, i.e., triglycerides of long chain fatty acids, would have been used, the tapa was analyzed for such oils. Small samples were submitted to hydrolysing conditions to release the fatty acids and then to esterifying conditions to convert them to methyl esters. The methyl esters were then separated by gas chromatography and identified by subsequent, on line mass spectrometry. Similar chromatographic peak patterns were found for seven specimens of Hawaiian tapa. They contained peaks, in consistent relative amounts, derived from the saturated fatty acids stearic and palmitic acids and from the dicarboxylic azelaic, suberic and sebacic acids. Natural oils tend to contain both saturated fatty acids and unsaturated ones, such as, oleic, linoleic and linolenic acids. Upon ageing the saturated fatty acids remain relatively unchanged but the unsaturated fatty acids are highly reactive. Oxygen attacks their double bonds causing both crosslinking between molecules to occur and oxidized radicals to form at the positions of the double bonds. Eventually these positions of unsaturation are oxidized to carboxyl radicals converting the original unsaturated fatty acids into shorter chained dicarboxylic acids. Hence chromatograms of aged oils no longer have peaks of unsaturated acid esters but rather of the esters of dicarboxylic acids derived from the unsaturated acids. In the observed chromatograms the ratios of methyl stearate to methyl palmitate peaks were consistent with those found in the oils of the kukui and kamani nuts. The kukui nut oil is relatively high in unsaturated fatty acids while the kamani nut oil is relatively unsaturated, hence the relatively high amounts of dicarboxylic acid found in the cloth would be consistent only with kukui nut oil having been used.

The deterioration therefore could be explained as resulting from the use of a highly unsaturated nut oil that resulted in 1) a high degree of crosslinking which led to

stiffness and 2) the development of a highly acidic condition, through oxidation, that leads to a general break down of structure resulting in friability.

The analysis of microscopic details is often a significant part of the examination of a work of art or an archaeological artifact. Electron beam microprobes or scanning electron microscopes equipped with X-ray detectors and proton microprobes have been extensively used for such analysis. In using such instruments one first most often focuses the ion beam on an area or on a specific particle and records the X-ray spectrum generated from the bombarded region. Having determined what elements are present, one then often adjusts the microprobe to respond to the X-ray of a specific element and scans over the microscopic section to determine where the element is located. By means of scans over individual linear traverses through a section, plots of elemental concentrations as a function of position can be obtained. By means of multiple, progressive raster scans over an area, so called dot matrix photographs can be obtained showing the distributions of individual elements throughout that area. Such raster scanning is of the type used to produce television images.

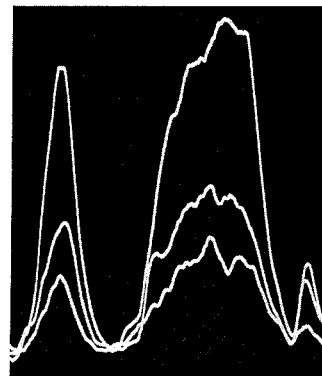


Fig. 8 Linear Scan through Lead-Tin Yellow II Particles

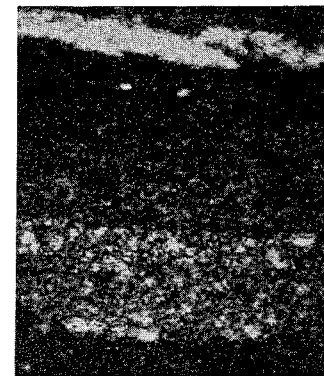


Fig. 9 Dot Matrix Scan for Arsenic in a Pigment Layer

An example of a linear concentration scan occurs in the positive identification of a particular pigment in an oil painting. Lead-tin yellow is an artist's pigment that was used in oil paintings during the period of the 14th through the first half of the 18th centuries. The historical knowledge of it had been lost. It was only through recent chemical analysis of pigment layers in paintings that its existence was discovered [12]. It occurred in two forms. One, lead-tin yellow I, was lead stannate, Pb_2SnO_4 , to which extenders, usually containing silica, were added. The other, lead-tin yellow II, was a compound of lead, tin and silicon, most probably $\text{PbSn}_2\text{SiO}_7$. Both pigments tended to contain lead, tin and silicon, but in one type the silicon was external to the yellow particles themselves and in the other silicon was an intrinsic part of the yellow particles.

Figure 8 shows superimposed linear microprobe scans for lead (greatest intensity) tin (medium intensity) and silicon (least intensity) over some yellow particles present in an oil painting cross section. The scans show that all three elements were present in the particles themselves and, hence, that the pigment present was lead-tin yellow II.

An example of a raster, dot matrix scan of a painting cross section is shown in Figure 9. The scan was for the element arsenic, and the layer that shows up as a light strip in the photograph was a bright yellow layer in the cross section itself. One was able to infer from the measurement that the yellow pigment in this instance was the mineral orpiment, an arsenic sulfide. One could confirm this, of course, by similarly scanning for sulfur.

One can achieve greater spatial resolution with a scanning Auger microscope than one can with an electron microprobe, because the Auger electrons generated are about 100 times less penetrating than are the X-rays generated by a microprobe. A very interesting use of scanning Auger microscopy to measure the diffusion of iron from ink lines in manuscripts into the paper upon which they were laid down was reported by Mc Neil [13]. Figure 10 shows an iron scan over an ink line in which regions of capillary diffusion of iron from the outer edges of the original line into the paper are observable. Figure 11 is a one-sided composite of such scans made on manuscripts ranging in date from 1272 to 1972. The key relating individual scan lines to manuscript dates is 1, 1972; 2, 1904; 3, 1857; 4, 1747; 5, 1457; 6, 1354; 7, 1272. It can be seen that there is a steady progression of diffusion of iron from the ink lines into the paper that correlates closely with time. In fact the correlation was found to be significant at the $P = 0.90$ level. Thus, one can see that such analytical measurements can be used to date old manuscripts.

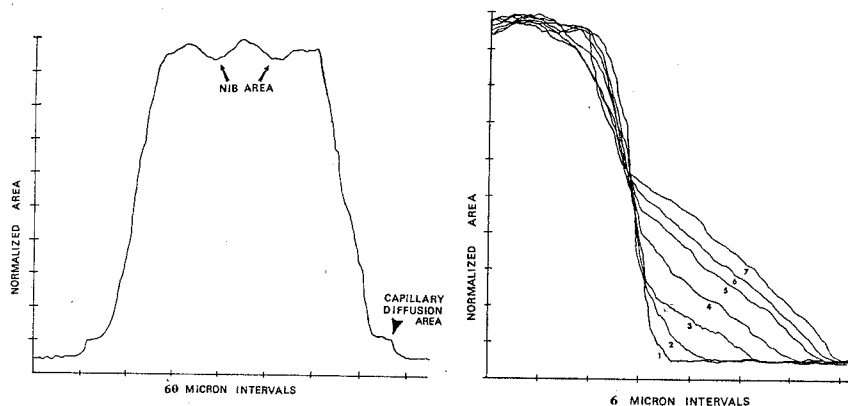


Fig. 10 Auger Scan for Iron over a Manuscript Ink Line showing Diffusion Edges.

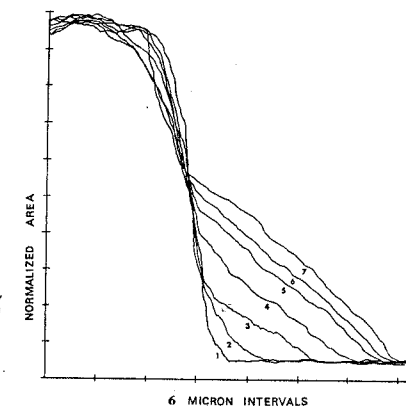


Fig. 11 Superimposed Diffusion Edges of Lines on Manuscripts of Various Dates.

Many more applications of compositional analysis to archaeological and art historical problems could be cited in which yet additional methods of analysis were used. New methods of analysis are being so applied almost as soon as they are developed. It is hoped that this brief survey will provide some overall feeling of the scope and purpose of such applications.

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