

Chapter 1

New Directions in Archaeological Chemistry

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This recent symposium on archaeological chemistry emphasized studies in new areas of interest to archaeologists and archaeological chemists. Not only are the traditional areas of metal, glass, pottery, and stone treated, but also archaeological soils, fibers, dyes, bone, connective tissue, DNA, and organic residues.

Shedding light on the past by means of scientific examination received great impetus when major museums began to establish laboratories for that purpose on their premises. For example, the work of Alexander Scott in the 1920's gave rise to the world-renowned laboratories of the British Museum. While museums were mainly concerned with examination of their own holdings, many university laboratories in departments of archaeology, anthropology and chemistry found ample work by examination of materials from excavations worldwide. Recent research in these laboratories has concentrated on ancient metals, stone, pottery and glass, as evidenced from the reports of the biennial international archaeometry conferences and specialized journals in the field (1-3).

Archaeological Chemistry

The modern field of archaeological chemistry arose during the first thirty years after World War II as a result of the development of instrumental methods of inorganic analysis, which made it possible to develop new areas in archaeological chemistry. The methods of choice over the years have concentrated on elemental analysis, whether by atomic absorption or emission, X-ray fluorescence, plasma emission spectroscopy, X-ray powder diffraction, neutron activation analysis or mass spectrometry. These methods have lent themselves to the analysis of stone and lithic artifacts, ceramic materials, glass and metallic materials. Many of the methods of analysis, such as lead isotope provenance studies of marble or elemental provenance studies of obsidian, have passed through several generations of development. Some of the methods survived the tests of validity and of utility. Some have disappeared from the scene, either because the methods had fatal flaws or they did not really solve archaeological problems. Inorganic methods continue to be improved upon and added to, and a large body of literature has developed in this area.

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The task of the archaeological chemist has become more complex than ever over the past decade. Once the domain of analytical chemists turned "amateur archaeologists," effective work in this area demands increasingly sophisticated equipment by way of advanced instrumentation, increased knowledge of statistical software packages for the assembling, processing and interpretation of coherent data-sets, increased interaction with members of related disciplines, awareness of the ever-burgeoning literature of archaeometry, archaeology and anthropology, and perhaps more important than ever, continual interaction and collaboration with members of related disciplines. Chemists working in this area must be aware of the fact that analytical data can be completely meaningless unless it is interpreted within the matrix surrounding the artifact or sample being investigated: professionally executed field work, well-documented excavation, proper sampling technique and meaningful scientific interpretation of the resulting data. Indeed, in the words of E. M. Jope (4), in order for any type of work in archaeological chemistry "to be effective, it must be collaborative. Integrations between excavators, investigators of excavated material, prehistorians and historians, and scientists of all sorts, is now growing, so that we are increasingly all one family seeking to present the past in a systematized and intelligible form."

The Present Symposium

While many of the goals of past volumes in this series (5, 6) coincide with the goals of this volume, namely, the mutual education of chemists, archaeologists and anthropologists in the use of new techniques on archaeological substrates and in the interpretation of data obtained therefrom, it is the choice of organic and biochemical substrates on the part of many of the investigators represented in this volume that makes this collection of papers unique. The solicitation of papers for this symposium contributed to a slant in this direction since only in very recent years has it been possible to analyze biological and organic materials with the significantly lower detection limits that enables these methods to lend themselves uniquely to solving some difficult archaeological problems.

Hence, the characteristic of the symposium represented by the papers collected in this volume was the virtual disappearance of many of the traditional materials normally reported on at archaeological and archaeometric meetings, namely, metal, pottery, stone and glass. For example, in *Archaeological Chemistry - III* (5), the proceedings of the Seventh Symposium on Archaeological Chemistry organized by the Division of the History of Chemistry's Subdivision of Archaeological Chemistry, fully two-thirds of the papers were devoted to inorganic materials, whereas only one-half of the papers in *Archaeological Chemistry - IV* (proceedings of the Eighth Symposium; 6) had inorganic materials as their subject. Of overwhelming interest to the contributors of the symposium that forms the basis of this volume were fibers, dyes, bone, collagen, archaeological soils, DNA analysis, and organic residues from a variety of artifacts including rock paintings and pottery. Two papers dealt with archaeological mineralized plant fiber. Three papers studied the identification of natural dyestuffs used for ancient textiles from Western and Eastern Asia. Ten papers dealt with archaeological bone and collagen, including dating, degradation determinations, analysis of lipid biomarkers, and quantitative measurements to reconstruct paleodiets. Six papers examined nucleotides in archaeological materials, including such technical difficulties as need for extraction, purification and isolation of high molecular weight fragments. The remainder of the papers reported on soil analysis, natural products, copper-based artifacts and pigments, and inorganic and organic residues on artifacts. Two papers each were presented on glass and metals; one paper each was presented on clay, flint, and obsidian. In summary, fully thirty-four of the forty-eight papers submitted for

inclusion in this symposium dealt with organic substances or artifacts, a complete inversion of the ratio of organic to inorganic materials studied in comparison with the symposium of 1982 (5).

A major part of the symposium was devoted to papers dealing with gaining information about the peopling of the New World. One paper dealt with the possibility that the use of radiocarbon calibration alone will never resolve the debate over the date that the first humans entered North America. Another paper described the development of a chrono-cultural tool for determining contemporaneity of artifacts during the first contacts between Europeans and native North Americans.

The range of methodologies used to study the archaeological artifacts and remains was very broad. Simple wet chemical techniques were used in several cases. The most popular spectroscopic method was Fourier Transform Infrared Microspectroscopy (FT-IR). Instrumental Neutron Activation Analysis (INAA) was also utilized in several instances. However, it became quite clear that the instruments of choice are presently those which can be coupled with mass spectrometry. Many papers utilized gas chromatography coupled with mass spectrometry (GC/MS), high performance liquid chromatography coupled with MS (LC/MS), GC/MS-SIM, where SIM = selected ion monitoring, GC/MS/MS and inductively coupled plasma/MS (ICP/MS). One paper demonstrated for the first time that mass spectrometry can be used in the direct chemical examination of nucleotide bases in ancient materials.

An important feature of the symposium was an accompanying pedagogical symposium designed to provide information to practicing chemists on some of these new techniques, and at the same time to provide information on some of the more exciting substrates of archaeological chemistry such as the "Iceman" recently found in the Alps.

We can learn a great deal from the make-up of this symposium. We learn that molecular archaeology is making great strides by utilization of sophisticated instrumentation. We learn that simple wet chemical techniques are still viable; we also learn that some archaeological problems are not susceptible of solution unless a battery of highly sophisticated instruments and data-set analysis software is available. We learn that organic materials can yield important information despite the fact that degradation has taken place over centuries and millennia. Indeed, through special techniques reported in this symposium, it has been shown that the formidable challenge of reconstructing the original composition of organic material from its present degraded condition is a problem susceptible of resolution. Finally, we can note in many instances the use of sophisticated statistical software packages that can help in extracting meaningful scientific and archaeological information from analytical data.

Inorganic Materials

The rapid development of sophisticated analytical techniques for elemental analysis following World War II opened the way to archaeological chemical investigations of materials susceptible to elemental analysis, namely, ceramic materials, glass, stone and metals. For many years, these materials constituted the major set of substrates studied by archaeological chemists.

Neutron activation analysis and instrumental neutron activation analysis (NAA and INAA) became the method of choice for analysis of ceramics because of an array of factors: whole sample characterization, capability of high precision multi-element qualitative and quantitative analysis, and small sample size, to name a few (7). The greatly improved successor to emission spectroscopy (ES), Inductively Coupled Plasma (ICP) spectroscopy, with its greater sensitivity and wider range of analytes, overlaps with NAA with respect to only six elements with the required levels of precision (8). This means, of course, that both methods are useful in developing more

broadly-based data-sets, but are virtually useless for comparison of data. Another powerful tool in the determination of the bulk chemical compositions of the clay bodies and glazes in ceramic materials is energy dispersive X-ray diffraction attached to a scanning electron microscope (9).

Many of the above-mentioned methods are also useful for the analysis of archaeological glass. However, electron-microprobe analysis (EMPA) and scanning electron microscopy (SEM) have been particularly useful because they are virtually nondestructive. Other methods such as ICPS and INAA are useful for analyzing unweathered glass, which is essential for valid comparisons between glass compositions. Glass analysis, in the past, has provided information regarding the sources of the raw materials used, the modification of glass colors, and the chemical characterization of glass products. Such information can provide the archaeologist with comprehensive data-sets susceptible to archaeological interpretation (10). Susan Frank has produced a comprehensive guide to archaeological glass in all of its aspects (11) and two excellent review articles by R. H. Brill (12) and D. Grose (13) summarize how modern chemical and physical analysis can reveal the sophisticated techniques of ancient Egyptian and Roman glassmakers. In chapter 2 of this volume, J. B. Lambert and co-workers utilize many of these techniques in analyzing 9th century Thai glass by ICPS in order to understand maritime trade patterns. In chapter 3 of this volume, R. G. V. Hancock, S. Aufreiter and J.-F. Moreau, using INAA as their analytical tool, compare the individual chemistries of three suites of turquoise glass trade beads with the previously established chemistries of well-dated beads from other archaeological sites.

Examination of stone and the lithic artifacts derived therefrom has usually taken the form of trace element analysis using many of the methods described above. Such analyses are very helpful in determining the sources of the raw materials, such as flint and marble, used to make artifacts (14, 15). Of even greater importance is examination of the factors that lead to erosion of stone and of chemical means that can be used to retard erosion. Threats to stone surfaces such as weathering, atmospheric pollution and attack by algae, fungi, mold and other microorganisms (16) is the subject of intense research at the present time. A fine review article by K. Lal Gauri summarizes some of the most promising approaches to this problem (17). Examination of stone also includes gemstones; NAA and other techniques have been used effectively to come to some understanding of a gem's religious, cultural and economic significance (18). A. R. Skinner and M. N. Rudolph, in chapter 4 of this volume, outline the possibility of using a relatively new dating technique, electron spin resonance (ESR), for determining the age of flint artifacts. They show that ESR has some advantages over the conventional technique, thermoluminescence (TL), but that some problems remain particularly in the area of sample selection. In chapter 5, F. R. Beardsley, G. G. Goles and W. S. Ayres summarize their INAA results on Easter Island obsidian in an attempt to trace the obsidian artifacts to their raw material source.

Analysis of metal artifacts by such methods as INAA and X-ray fluorescence (XRF) has been very valuable in determining trace metals embedded in a parent metal, giving valuable clues to metal provenance. Lead isotope ratios has also been valuable in provenance studies, and SEM has given insights into metal-working technology (19-21). In chapter 6 of this volume, J.-F. Moreau and R. G. V. Hancock, using INAA to determine eight elements in 500 copper based artifacts, show how these measurements allow them to assess the degree of homogeneity of these artifacts at the intra-site level as a means of determining which parts of an archaeological site may be contemporaneous. In chapter 7, A. A. Gordus and I. Shimada examine the gold-silver-copper ternary alloy contents of gold objects from an unlooted Peruvian gravesite. Using NAA and EMPA, they are able to show that surface depletion of copper and consequent enrichment of gold and silver were not deliberate, but the result of the

repeated hammering-annealing required to produce the thin gold sheets used for the construction of the objects. G. F. Carter, in chapter 8, continues his study of the chemical composition of Roman coins using XRF as his method of choice. This analysis allowed undated coins previously estimated to have been struck between 15-16 A.D. and 22-23 A.D. to be confirmed. M. V. Orna, in chapter 9, shows how, in the Middle Ages, metallic copper was used to produce blue pigments that in some instances continue to defy characterization. Finally, in chapter 10, R. H. Tykot and S. M. M. Young summarize the archaeological applications of ICP/MS to stone and metal artifacts.

Archaeological Soils

Analysis of archaeological soils has historically centered around phosphate analysis. Phosphorus, in the form of phosphate, is a consistent indicator of human activity since its concentration increases through the life chain because of its relative chemical immobility. Phosphate analysis can therefore be used to detect the sites of human habitation even when all other traces of such habitation have disappeared (22). It can even be used, but with considerably more caveats, for the detection of bone that has virtually disappeared, leaving behind only a slight darkening of the soil known as a silhouette (23). A fairly recent critique of the use of soil phosphate analysis in archaeology (24) warns workers in this area to be aware of the fact that any archaeological site is dynamic and subject to change. Hence, phosphate could have been deposited either before or after settlement, or the general deposit of phosphate may not distinguish between human and higher animal use. In chapter 11 of this volume, H. Chaya describes a method for determining total phosphorus at an Aleutian Island site occupied by marine hunter-gatherers over a 1500 year period using molybdivanadophosphate color development rather than the more conventional molybdenum blue method. In chapter 12, another wet chemical technique is utilized by L. Barba, L. López, A. Ortiz, K. Link and L. Lazos in their analysis of residues on the lime plaster floors at the Templo Mayor of Tenochtitlan, and important Aztec archaeological site. From these analyses, they propose to be able to infer or reconstruct the ritual activities that took place at that site. In this case, these workers assume that the lime plaster floor, or the archaeological soil, was the baseline location for the deposition of other materials. Another departure from the conventional treatment of archaeological soils is the work of R. P. Evershed, P. H. Bethell, J. Ottaway and P. Reynolds in chapter 13. They employ GC/MS-SIM to provide a very sensitive and selective means of analyzing for characteristic steroidal marker compounds that can confirm sites of suspected cess-pits and latrines. In each of these cases of investigating an archaeological soil substrate, the analytes, the methodologies and the kinds of information sought were different. The advent of extremely sensitive and selective analytical tools, such as those used by Evershed and co-workers, will allow extraction of information from such substrates that was once impossible to obtain.

Organic Materials: Fibers and Dyes

Organic analysis has generally required larger amounts of materials for structure proofs by nuclear magnetic resonance (NMR), although mass, electronic and vibrational spectroscopies were successful in addressing many problems in the fields of organic dyes and foodstuffs. The development of solid state NMR methods in the 1970s finally enabled that technique to be applied to insoluble organic materials as well. Organic materials now may be analyzed with the same degree of success as enjoyed by inorganics two or more decades ago. The methods must pass through the same evolutionary path that tests their validity and utility. Among the organic materials of

most interest to the participants in this symposium were fibers and dyes. Archaeological textiles may contain information regarding degradation, mineralization or other forms of alteration that can eventually lead to greater understanding of prehistoric environments and cultures. Elemental distribution (25) and isotope measurements (26) are often helpful in identifying and dating fibers. Fibers are rarely left in their raw natural state in use: they are normally dyed. The identification of these dyes can often be the beginning of a fascinating journey into history (27) and into the cultural and social significance of dyes (28).

In chapter 14 of this volume, R. D. Gillard and S. M. Hardman explore the mineralization of cellulosic and proteinaceous fibers through a laboratory simulation with oxygenated aqueous solutions. Using FT-IR microscopy they show that traces of organic material can survive long-term burial and even permit their identification under appropriate circumstances. H. L. Chen, D. W. Foreman and K. A. Jakes, in chapter 15, also study mineralization of fibers using XRD techniques to study the fibers' microstructure in order eventually to understand the mechanism of organic polymer degradation and replacement of the fiber by inorganic copper compounds. In chapter 16, K. A. Jakes and L. R. Sibley use IR spectroscopy in a different manner to study the cellulose, lignin and hemicellulose content that distinguishes types of fibers from one another. The next two chapters deal with the Shroud of Turin, a textile artifact that is associated by many with the suffering and death of Jesus Christ. A. Adler, in chapter 17, reviews the controversial status of the Shroud, particularly the nature of the image of a wounded human body that can be seen on it. In chapter 18, D. Kouznetsov, A. Ivanov and P. Veletsky highlight the inherent uncertainties of radiocarbon dating, particularly with respect to variations in conditions external to the artifact in question, indicating how this fact led them to question the accepted radiocarbon date of the Shroud of Turin. In their work, they devised a laboratory model to simulate the fire conditions to which the Shroud was subjected at Chambéry in 1532. Their results show that radiocarbon ages of experimental textile samples incubated under fire-simulating conditions are subject to notable error due to incorporation of significant amounts of ^{13}C and ^{14}C atoms from external combustion gases into the textile cellulose structure. They also take into account the known phenomenon of biological fractionation of carbon isotopes by living plants which can lead to enrichment of a textile by ^{13}C and ^{14}C isotopes during linen manufacture. Chapter 19 is a rebuttal to the Kouznetsov, et al. paper by a group at the University of Arizona headed by A. J. T. Jull. Jull and co-workers were members of the team that performed the radiocarbon dating on the Shroud of Turin in 1989 and found that the artifact had a carbon date of late-13th to mid-14th century, the time period when it first appeared in the historic record. Jull claims here, as he did at the original symposium, that the work of Kouznetsov, et al. is flawed since the Arizona team did not achieve similar results in their own fire-simulating experimentation. Editorially speaking, we must observe that the Arizona tests did not mimic the Kouznetsov tests since several of the experimental reactants were not present. These two papers are placed back-to-back in this volume to enable readers to compare them and draw their own conclusions. In chapter 20, the Kouznetsov team examines cellulose chains in archaeological textile remains, noting that they can contain a significant number of chemically modified β -D-glucose residues. Their work, using a capillary zone electrophoresis-mass spectrometric approach, shows a correlation between cellulose alkylation extent and calendar age of the textile samples tested. Their results suggest that if cellulose alkylation is the consequence of microbial activity, this phenomenon could be the basis of a new and efficient dating technique, at least among samples taken from a single site and subjected to a similar environment. In the final chapter in this section, chapter 21, Z. C. Koren discusses the application of high performance liquid chromatography (HPLC) to the identification of the natural

dyes, anthraquinonoids, flavanoids and indigoids, found in a variety of archaeological sites as much as 3000 years old.

Biological Materials: Archaeological Bone, Connective Tissue, DNA, Radiocarbon Measurements

Biochemical analysis began with isotopic measurements on bone collagen to obtain dietary information. Ancient human diet also can be inferred from inorganic analysis of bone. For example, from a simple direct argument about strontium levels in flesh, strontium levels of bone can provide information about meat intake (29). Stable carbon isotope analysis of bone and connective tissue is also emerging as a powerful tool in diet reconstruction (30). For example, carbon isotope values can distinguish between C₃ and C₄ type plants in the terrestrial food web. In chapter 22 of this volume, P. T. McCutcheon discusses the uses of TL and thermogravimetric analysis (TGA) to date bone mineral. In chapter 23, J. H. Burton points out that while bone strontium faithfully reflects the dietary Sr/Ca ratio, other factors besides trophic-level significantly affect this ratio. He also discusses the cautions one should use in interpreting the Ba/Ca ratio in bone as well. D. M. Greenlee, in chapter 24, shows that the combined techniques of backscattered electron imaging and EMPA can be used to examine archaeological human bones from different post-depositional environments. The bones were shown to have different levels of structural preservation and highly variable elemental compositions relative to modern bone. Potential criteria for identifying the diagenetic processes involved and for recognizing diagenetically unaltered areas are also discussed. In chapter 25, N. J. van der Merwe, R. H. Tykot and N. Hammond point out that since the relative contributions of the protein, carbohydrate and lipid portions of the diet to bone collagen and bone apatite are still not fully understood, it is necessary to perform isotopic carbon analysis on both tissues for proper dietary reconstruction in all but the simplest food webs. They also assert that analysis of the flora and fauna available for human exploitation may be equally important. In chapter 26, A. M. Child discusses the effects of microbial decomposition on the rate of aspartic acid racemization in mineralized collagen by measuring the degree of racemization after a prolonged incubation period of sterile modern pig bones inoculated with bacteria and fungi.

The methods of molecular biology now may be applied to genetic remains of plant and animal organisms. These latter methods, based largely on the polymerase chain reaction (PCR), are in their infancy as applied to ancient organisms. Biological contributions will assume a prominent position in this field as methods become more sophisticated and smaller samples can be effectively examined. Studies on even very degraded fractions of mitochondrial DNA have allowed biochemists and molecular biologists to trace migrations and matings of various species over many centuries, thus shedding lights on population patterns and closest genetic links of present species with past species of living things (31, 32). In chapter 27 of this volume, M. W. Rowe and M. Hyman utilize PCR and phylogenetic analysis to aid in the identification of the organic binder and vehicle used in the 3000-4000 year old rock paintings (pictographs) painted on shelter walls in Seminole Canyon, Texas. The ultrasensitive method of PCR was essential for this analysis because of the seriously degraded small fraction of DNA that remained after so many centuries. PCR amplifies DNA and can produce millions of DNA copies from only a few enduring DNA fragments, thus enabling the replicated DNA to be sequenced in order to derive the requisite information. The sequences obtained reveal that the organic matter in the paintings was definitely of mammalian origin. In chapter 28, R. Vargas-Sanders and Z. Salazar isolated and characterized high molecular weight DNA fractions from bone remains of Mexican prehispanic populations. In chapter 29, M. W. Rowe and M. Hyman report on the development of

a technique to remove organic carbon selectively from ancient pictograph paints without contamination from the mineral carbon in the rock substrate, mineral accretionary coatings or atmospheric carbon dioxide. Their technique is generally applicable to any pictographs which had organic matter added to the paints. C. M. Batt and A. M. Pollard, in chapter 30, demonstrate that questions concerning the earliest date that humans entered North America may not be answerable by radiocarbon dating alone. In chapter 31, D. L. Kirner and R. E. Taylor discuss techniques using accelerator mass spectrometry (AMS) whereby they can overcome the problem of background contamination in radiocarbon dating, thus opening the door to the use of microsamples.

Conclusion

While the papers contained in this volume do not cover all of the innovative work taking place at this moment in archaeological chemistry, they are a representative sample of such work and provide an overview for the interested archaeologist or chemist. In addition, a very substantial bibliography for each of the research areas discussed herein provides the reader with further material for study.

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