

6. Ionizing radiation in archeometry and history of art

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Introduction

Looking through any recent encyclopedia, it is quite common to find a more or less detailed explanation of the term "archeology". Thus, for instance, in *The Academic Dictionary of Foreign Words* [1], archeology is defined as a "historical science making use of material finds to study the oldest cultural and social history of mankind. The entries that follow in alphabetical order are "archeomagnetism", "archeopteryx", and so on. Also other encyclopedias follow the same order of items, as, e.g., [2]. However, "archeometry", the word used in the title above, is missing in all of them. And yet, archeomagnetic dating is one of the important methods used in archeometry. From April 22nd to April 26th 2002, Amsterdam, the Netherlands, hosted an International Symposium on Archeometry, 33rd in order, and, since 1958 there has existed an international journal on "Archaeometry". As is evident, this is a rather recent branch of science, but no hot issue at all, and so the encyclopedias have been slow to respond. But, what, then, is "archeometry" all about?

For many years now, it has been hardly sufficient in archeological studies to investigate the prehistoric sites in the classical way and to study only the material sources. Nor can the art historians' experience provide and find all the facts about the place and time of origin of a find, the production processes, or a later story of works of art if they are not properly documented in some written source. So, for over half a century, a significant support to these facts has been the study of archeological finds and works of art by methods of natural sciences, i.e., physics, chemistry, biology, biochemistry, metallurgy, geology, and others, their importance becoming more and more significant. This study added new knowledge to our treasure house and helped to develop interdisciplinary cooperation between archeologists, natural scientists, and historians, supplying also valuable information for restoration of works of art. Thus, finally, a new branch of science was born, with a name referring both to the remote past and exact measurements.

As archeometry was making advances, it became possible to date various organic and inorganic materials by methods such as radiocarbon dating,

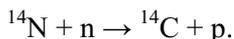
dendrochronology¹, thermoluminescence, optically stimulated luminescence, and, as mentioned above, archeomagnetism, etc. Thus it is possible to learn more about the way of life and the diet of ancient nations and tribes through the analysis of human and animal remains, scraps of organic materials and wastes. For a wide spectrum of works of art and objects of everyday life physical and chemical analytical methods help to study materials, production technologies, places of origin and trade routes of old. Exact evaluation methods of aerial photography are helpful in assessing the extent of old settlements and in detecting new sites of archeological interest. So, all that has been mentioned is what constitutes "archeometry"; it may be its interdisciplinary character or lack of interest in science generally that explain why "archeometry" has no entry of its own in encyclopedias. Despite this, archeometry is no less interesting or less important for extending man's knowledge.

We will now attempt to explain several methods and examples and show what results can be obtained in applying science to the study of historical monuments and works of art. Archeometry frequently makes use of ionising radiation methods (see, e.g., [3]), which are also the author's main concern. That is also why some of these methods will be explained in more detail, being illustrated by examples from all over the world. This should by no means denigrate the studies performed in the Czech lands generally, or at the Czech Technical University (CTU) in Prague specifically. By the way, Faculty of Nuclear Sciences and Physical Engineering of CTU has founded a laboratory specialising in works of art studies affiliated with the Department of Dosimetry and Application of Ionising Radiation. Some of its findings can be found in [4].

Radiocarbon dating

Radiocarbon dating is probably the best known method of archeometry, even older than the term itself. Based on the study of cosmic radiation effects on the Earth's atmosphere, it was developed in the latter half of the 40's by Professor Willard F. Libby, awarded the Nobel Prize in chemistry for this invention in 1960. Cosmic radiation is responsible for many nuclear reactions resulting in continuous production of radioactive nuclides. The most important and most frequently represented are ^3H , the heaviest isotope of hydrogen, and ^{14}C , one of the carbon isotopes, produced when atomic nuclei of atmospheric nitrogen react with neutrons, emitting at the same time a proton

¹ Dating based on the sequence of tree rings.



The ^{14}C half-life is 5,730 years, and, therefore, there is a limit to its accumulation in the atmosphere. Assuming that the long-term cosmic ray flux reaching the atmosphere had been constant², an equilibrium necessarily developed, i.e., the amount of ^{14}C due to cosmic radiation became balanced by its loss due to radioactive decay³. Carbon in the atmosphere is incorporated into carbon dioxide taken in by living organisms, plants, as well as animals, and even in them the radioactive ^{14}C and ^{12}C and ^{13}C , the stable isotopes of carbon, will eventually be in equilibrium. On the death of a biological organism, the flow of ^{14}C will stop and upset the equilibrium. The carbon present in the body at the moment of its death will remain there without any metabolism going on. Due to its radioactive decay, the amount of ^{14}C will gradually decrease according to the equation

$$C(t) = C(0) e^{-\lambda t},$$

where $C(0)$ is equilibrium concentration of ^{14}C in the body at the moment of death, $C(t)$ its concentration after time t since death of the body in question, and, λ is the ^{14}C decay constant. The value of $C(0)$ can be obtained from the "present" samples⁴; λ is a physical constant, so time t can be obtained by measuring the actual concentration $C(t)$ and performing a simple calculation. In principle, this method is viable in all materials of organic origin; exceptionally, however, it can be used even for dating inorganic materials that incorporated atmospheric carbon at the time they originated, most often in the form of carbonates (e.g., stalactite and stalagmite formations), upon which the exchange stopped. Measuring concentrations $C(t)$ is not a simple matter at all.

W. F. Libby and some of his successors measured ^{14}C concentrations on the basis of its radioactive decay and emitted radiation. However, ^{14}C is a beta source, emitting rather low-energy electrons; moreover, the samples of materials measured contain ^{14}C of extremely low activity. Consequently, it has to be extracted from the samples and transferred directly to the detecting medium in the ionising radiation detector. With a gas-filled proportional

² This assumption is not quite exact; in fact, when evaluating the results of radiocarbon dating, the change in cosmic ray flux with time has to be corrected.

³ Its amount is negligible compared with stable isotopes of carbon; i.e., only approximately 0.000000001 % of natural mixture of isotopes.

⁴ Due to the release of large amounts of ^{14}C into the atmosphere during nuclear tests, and due to the large emissions of non-active carbon isotopes into the atmosphere when burning fossil fuels after the Industrial Revolution, the equilibrium is now upset. Therefore, no present organic material can be utilised, and so term "present sample" refers to an exactly defined standard kept in the National Institute for Standards and Technology in the USA.

detector, carbon is usually transferred into CO₂ or acetylene; with liquid scintillators it is changed into benzene, which means that at least a part of the dated object is destroyed (usually, the loss amounts to several units or tens of grams). With more valuable objects, this may even be a limiting factor for using this method. Moreover, the detector design is quite sophisticated and may present a problem as how to minimise the content of natural radionuclides in the detector material used, because the background should be very low⁵. For the measurement results to be reasonably exact, the time required for each sample is to be of the order of tens or even hundreds of hours.

Since the 70's of the last century, another detection method has been pushing through, namely **the Accelerator Mass Spectrometry (AMS)**. It is based on direct counting of ionised carbon atoms from the sample measured. A beam of ionised atoms accelerated in the ion accelerator is deflected by a magnetic field from its path. Lighter ions are deflected more easily, and, therefore, it is possible to separate carbon isotopes of various mass and measure their proportional representation. AMS sensitivity is several orders higher than that of ¹⁴C radioactive decay detection or of the "classical" mass spectrometry, and, so, the sample size and measurement time can be substantially reduced (Table 2). This can be demonstrated by the following example: 1 mg of carbon 5,000 years old contains about 20 mil. ¹⁴C atoms. To count 10,000 pulses by beta detection, corresponding to a standard deviation of 1 percent, the measurement would take 4 years. With the accelerator, to count 10,000 ¹⁴C ions from a sample to obtain the same statistical error would take less than one hour. The disadvantages of this method are the high costs of the accelerator and the laboratory equipment.

Table 2: Typical sample size necessary for dating when using ¹⁴C radioactive decay detection (RDD) and AMS (according to [5]). The data tabulated are tentative only and may vary from laboratory to laboratory.

Material	Dry mass (g)		
	RDD (optimal)	RDD (minimal)	AMS
Wood, charcoal	8 – 12	1	0,005 – 0,010
Carbonates	35	5	0,015
Peat	5 – 10	1	0,100 – 1,000
Bones	100 – 200	20 – 80	1
Lake sediments	30 – 100	10 – 20	1

⁵ *I.e., it must have a low detected pulse rate, its cause being other than detection of radiation from the sample measured.*

One of the much-disputed applications of AMS is dating the so-called **Holy Shroud of Turin**. It is a piece of linen cloth 4.36 m by 1.10 m, kept in St. John's Cathedral in Turin, believed by many scientists and church authorities to have been used to wrap Christ's body after the Descent from the Cross. It is one of the most precious church relics. The Shroud shows a negatively imprinted dark brown fuzzy silhouette of a man's body (see Fig. 6), but only the rusty blood spots are well contoured. The issue of how the imprint could originate is still unresolved.



Fig. 6: Christ's face from the so called Holy Shroud of Turin (a negative – the Shroud shows a negative silhouette of the body, so the picture is positive).

In 1988, a strip 70 mm long and 10 mm wide was removed from the Shroud and cut into three pieces; they were sent to AMS laboratories at Oxford, Zurich, and the University of Arizona at Tucson to be dated. Their results, reaching a confidence level of 90 percent, indicated dating between 1290 – 1360 A.D., which is in good agreement with the year 1353, i.e., the earliest time the Shroud had been recorded in historical documents. Never-

theless, its authenticity is still contested and radiocarbon data questioned, e.g., by arguing that the amount of later date carbon may be due to candle soot or oil lamps or bacteria and microorganisms.

Dating the iron crown of Charlemagne can provide another example. The origin and age of the crown, kept in the Monza Cathedral, Italy, are also uncertain. However, historical sources place the crown's origin within an interval of several centuries. In 1996, it was found that the precious stones in the crown are set in a mixture of clay and beeswax, permitting thus radiocarbon dating. The only possible technique to apply was AMS, the amount of material being so scarce. Dating placed the crown to years 700 – 780 A.D., which agrees with the known date of Charlemagne's coronation (800 A.D.) [7].

Thermoluminescence dating

Radiation-induced thermoluminescence (TL) is a phenomenon closely connected with electron transitions between energy levels in inorganic solids, namely in ion crystals. This can best be shown by a brief and simplified model.

Mutual interactions between crystals of an atom cause energy levels to extend to energy bands, which can be occupied by electrons in the atom. The last occupied band, i.e. valence band, is separated from the conduction band – where free electrons can move – by the forbidden gap. In an ideal crystal, the forbidden gap cannot contain any electrons. In a real case, however, various impurities and irregularities in the crystal lattice can create local energy levels even in the forbidden gap, and the local levels are being occupied by electrons. Some of these levels are in fact "traps" which – under the action of ionising radiation – capture electrons which will be released only after some supply of energy from the outside, as, e.g., after heating. In the subsequent transitions between various energy levels, these electrons can pass through the so-called luminescence centres, electromagnetic radiation being released, frequently in the region of visible light. The dependence of emitted light intensity on temperature is referred to as glow curve. The number of electrons captured in the traps is proportional within a wide range to the dose of ionising radiation, and the luminous flux is proportional to the number of captured electrons; consequently, the glow curve maxima or the area below it are proportional to the dose. Therefore, knowing the TL sensitivity of a given material, i.e., its TL response to unit dose, it is possible to obtain the dose the material was exposed to by measuring the light output at heating. This phenomenon is widely used in dosimetry of ionising radia-