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A survey on innovative dating methods in archaeometry with focus on fossil bones

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ABSTRACT

Recently proposed innovative methods for dating archaeological finds reported in the literature are reviewed, together with the researches carried out in this field by our team, using several instrumental techniques (sensor, biosensor, electrochemical, thermal-analytical, and so on). In this framework, particular attention was then focused on examining the main currently adopted methods for bones dating. Lastly, the possibility of using thermogravimetry coupled to chemometrics for differentiating, quickly and inexpensively, finds of very ancient human fossil bones (several thousand years BC), from less ancient ones (few hundreds of years before and after Christ) is illustrated, together with a thorough discussion of the criteria (i.e., the collagen-carbonates content ratio, or the different types of carbonate) this approach is based on.

Contents

1. Innovative dating of archaeological finds, using sensors, biosensors, other electrochemical methods, thermal analysis, biochemical clocks and beyond

As it is well known, the fossil dating is essential to develop a chronometric scale applicable in sketching a geological history of the stratigraphic classification of rocks and for dating geological events. In practice, the fossil dating can offer a time-scale for relative age determinations and for world-wide correlations of rocks. This kind of relative dating method can be considered a rather old standard approach. However, since the 60s of the last century, absolute dating methods, particularly radiometric, have also been developed. The majority of them is, in fact, based on the decay of radioactive isotopes, either the so-called "primordial" ones, such as ^{238}U, ^{230}Th, or ^{40}K, or of so-called "continuous creation" radioisotopes, such as ^{14}C. Despite effectively suffering from numerous drawbacks, also these methods have now become classical approaches, like the rest of other methods now very popular, such as the Fission Track, Thermoluminescence, or Optically Stimulated Luminescence, Electron Spin Resonance, Dendrochronology, Obsidian dating, Amino acids racemization and Archaeomagnetism. For these techniques, which have become well established, the applicability range and the accuracy are rather well characterized (even if in some cases the different sources are only partially agreeing) and are summarized in Table 1. Of course, in the meantime, several researchers have attempted to develop, and then to propose, other approaches, different from those mentioned, certainly still much less known, and not fully investigated in terms of their applicability characteristics, and received with greater or less attention, for several reasons.

For example our research team has been developing and testing instrumental chemical method and chemometric techniques in order to meet different needs, prompted by archaeologists and paleontologists, concerning dating, differentiation, classification, or the characterization of different types of archaeological, paleontological, or cultural heritage findings. These objectives have been addressed with different approaches: for instance, making use of biosensing, electrochemical or enzymatic methods. Among them, it is worth mentioning a biosensor method [31,32] for the dating of wood or paper finds, based on the construction of an amperometric biosensor, assembled using a Clark-type gaseous

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Table 1
Summary of the characteristics of the classical dating approaches in archaeometry

Method	Chronological interval (years)	Accuracy (Relative error %)	References
Pb-U series	10^2-5×10^3*	25–75%	[1–6]
	5×10^3-5×10^4	8–25%	
	5×10^4-3×10^5	2–8%	
	3×10^5-10^6	8–25%	
Potassium-Argon	10^3-10^4*	>75%	[1,3,4,7]
	10^4-5×10^4	25–75%	
	5×10^4-10^5	8–25%	
	10^5-10^7	2–8%	
Fission track	3×10^2-10^4*	>75%	[1,3,4,8,9]
	10^4-5×10^4	25–75%	
	5×10^4-3×10^5	8–25%	
	3×10^5-10^7	2–8%	
Radiocarbon	10^2-5×10^2	>8%	[1,3,4,10–21]
	5×10^2-2×10^3	2–8%	
	2×10^3-5×10^4	<2%	
Thermoluminescence/ Electron spin resonance	10^2-5×10^3	>75%	[1,3,4,22,23]
	5×10^3-3×10^4	25–75%	
	3×10^4-2×10^6	8–25%	
	2×10^6-10^7*	25–75%	
Obsidian hydration	10^2-4×10^5	8–25%	[1,3,4,24,25]
	4×10^5-10^6*	25–75%	
Dendrochronology	10^2-6×10^3	<2%	[1,3,4,26]
Archaeomagnetism	10^2-3×10^3	8–25%	[1,3,4,27]
	3×10^3-8×10^3*	25–75%	
Palaeomagnetism	3×10^4-9×10^4*	25–75%	[1,3,4,28]
	9×10^4-10^7	8–25%	
Amino acid racemization	10^2-10^4	25–75%	[1,3,4,29]
	10^4-4×10^5	8–25%	
	4×10^5-4×10^6*	25–75%	

* Indicates extended range under special experimental conditions [30].

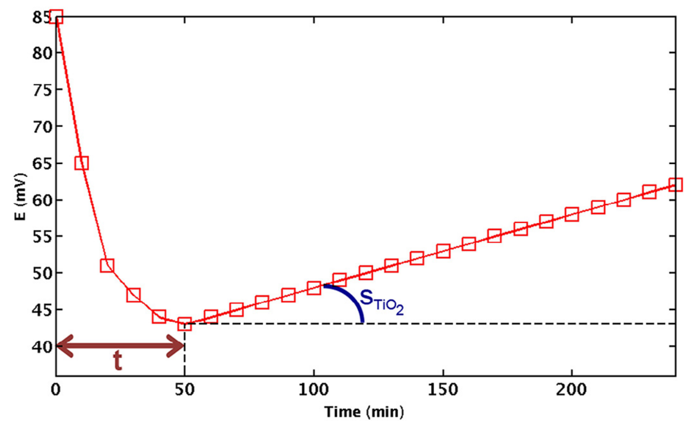

Fig. 1. Definition of the environmental persistence through the photosensor response. The environmental persistence (P_{env}) is defined through the slope (s_{TiO2}) and the delay time (t) as: $P_{env} = t/s_{TiO2}$.

diffusion amperometric electrode and the enzyme glucose oxidase, immobilized by carbodiimide (N- (3-propyl-dimethylamino)-N'-ethylcarbodiimide) on a standard disk, cut from the specimen to be dated.

The principle of the method is the following: since it has been shown [33] that the more ancient a cellulosic sample is, the greater the number of carboxy groups contained in it, and, therefore, the more the molecules of a given enzyme (e.g. glucose oxidase) which can be covalently immobilized on it, with a simple method, such as that of carbodiimide. Accordingly, if one prepares a disk of cellulosic specimen (wood, cloth, paper) with a standardized size and weight, the older the sample is, the higher the amount of glucose oxidase covalently immobilized on it will be. This diskette is then fixed on the head of an amperometric electrode (Clark-type), which is then immersed in a buffer solution, to which a fixed quantity of the enzyme substrate (i.e., glucose) is added. As a consequence of the enzymatic reaction, which consumes the oxygen in solution, a decrease of the current intensity through the electrode will be observed; such decrease is proportional to the amount of immobilized enzyme, and, hence, to the number of carboxylic groups present on the find, therefore to the sample's antiquity. For the same types of objects, but also for plant tissues, a different enzymatic method was also experienced by us [34], introducing some innovations to the one originally developed by S. Kouznetsov [33], and based on the enzyme SAMT (S-adenosylmethionine-transmethylase), capable of catalyzing a reaction of transferring methyl groups, present on a ancient cellulosic find, to a specific acceptor molecule. In this enzymatic reaction, adenosine, which can be easily determined with different instrumental methods [33–35], is generated and the antiquity of cellulosic analyzed find evaluated on the basis of the quantity of adenosine checked. In detail, the cellulosic material, in the presence of the enzyme SAMT, S-adenosylmethionine (SAM) and Tetrahydropholic acid (THFA), is converted to demethylated cellulosic material, adenosine and omocysteine.

Another dating method, proposed by our group, consisted in the development of a potentiometric photosensor, based on the catalyst titanium dioxide (TiO_2) and a platinum electrode [36]. A potentiometric curve is obtained by means of this sensor, during the photodegradation of a cellulosic artifact, by irradiation with UV light ($\lambda = 350$ nm) in a reaction cell. In particular, due to the chemical species that are formed in solution during the catalytic degradation of the sample under investigation, a variation of the electrode potential, which occurs according to a characteristic pattern (see Fig. 1), which allows to measure a parameter called "environmental persistence", is produced; the latter is put in relation with the aging state and, then, with the antiquity of a find, especially cellulosic [36–38].

On the other hand, the use of cyclic voltammetry, has recently allowed not only to determine the amount of lignin [39], but also to make a short archaeometric curve of the same lignin artificially aged [39]. These cited methods have dealt especially with the dating of cellulosic finds.

It is clear that several different electrochemical methods have also been proposed by other authors in the literature.

From a general point of view, all classical Faradic electrochemical methods are very sensitive techniques for identifying and determining a lot of electroactive specie present in the samples. They are able to carry out speciation studies, providing also a complete description of the state of oxidation of the ionic species contained in the finds. Also non-Faradic electrochemical methods, for instance conductometric techniques, have been extensively used, in several occasion, e.g. for monitoring the content of salts removed during water immersion treatments of ancient ceramic remains and archaeological potteries. In this way the electrochemical techniques, being able to characterize in detail the materials concerned, are certainly able to guide and assist the dating of archaeological finds, even when this is done with methods more specific for this purpose.

In addition to these general electroanalytical methods, recently it has been evidenced that the chemical evaluation of the extent of corrosion in archaeological artifacts can provide insight into the duration of the corrosion process, so that the latter process, by using several simplifying assumptions, can be used to estimate the antiquity of a metal archaeological find. Reich et al. [40] firstly used measurements on the Meissner fraction in the superconducting state to evaluate the mass of the uncorroded metal sample, contained in the find, in order to estimate the age of the archaeological lead artifacts. In brief, lead metal, at room temperature exhibits diamagnetic susceptibility of the same order of magnitude