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The Enzymatic Dating of Ancient Heritage: Comparison Between Two Methods on Terms of Uncertainty

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Abstract

Two enzymatic methods for dating cellulosic materials were set up and tested on both real and artificially aged matrices.

Performances were compared with particular attention paid to the uncertainties of the evaluation. So by applying the propagation rules we compared the two methods concluding about which one of the two considered is more reproducible, so that the uncertainty range is narrower.

Introduction

The dating of ancient founds is one of the bet of science. On one hand science looks at stabilising materials in order to fight their ageing, but on the other one the marks of the ageing are those which allow to be informed about the evaluation of the age of the founds. This double attention corresponds to two different fields of chemistry of cultural heritage, that one of protection and conservation the former, of dating the latter. By this way the dating is a very complex analysis for which radio carbon methods are surely the most reliable ones. But alternatives to them are traditionally proposed and continuously set up. We have applied our experience on enzymatic methods to dating and characterised these methods for the analytical performances.

Materials & Methods

For data collection was used: Amel mod. 360 dissolved oxygen meter equipped with an Amel 332/P oxygen electrode (Amel, Italy); Clarus 600 GC/Mass Spectrometer (Perkin Elmer, USA); Veterometer QUV Weathering Tester - Model QUV/Spray (Q -Panel LAB, USA)

Analytical procedures

During ageing, due to oxidation processes, an increase of carboxylic group occurs on cellulosic materials as well as a decrease of methyl groups. Both the processes were used for analytical purposes as follow. The first dating method (biosensor method) bases on the measure of the immobilised enzyme activity of glucose oxidase (GOD) using carbodiimide as a bond between carboxyl groups formed on the degraded cellulose and the protein amino groups of GOD[1,2].

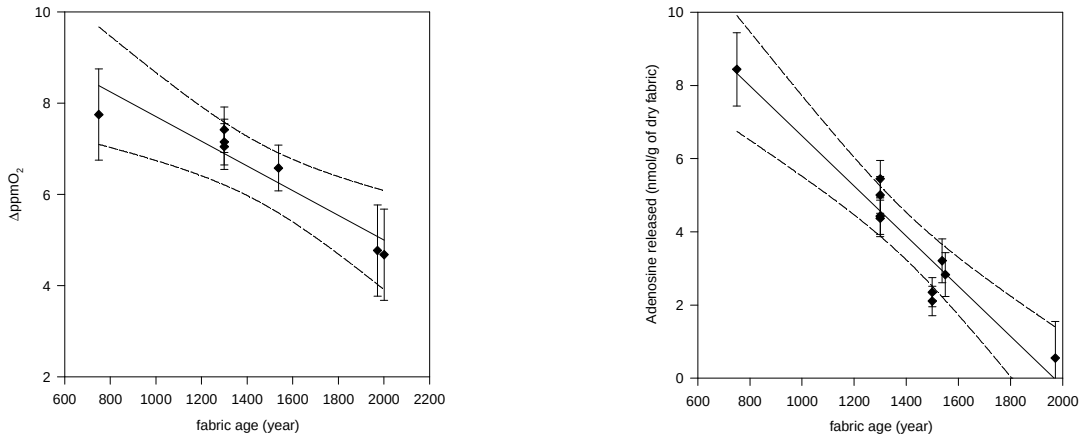
The oxygen consumption relative to the following enzymatic reaction can be measured by a Clark oxygen electrode

$$\beta - \text{glucose} + O_2 + H_2O \xrightarrow{\text{GOD}} \text{gluconic acid} + H_2O_2$$

The second method (SAMT method) bases on the GC-MS determination of adenosine produced through the enzymatic reaction by s-adenosylmethionine-transmethylase (SAMT) in presence of s-adenosylmethionine (SAM) and tetrahydrofolic acid (THFA) as enzymatic cofactor[1,2].

Results

Using dated samples, both the two enzymatic methods allows us to obtain data useful to construct the archeometric curves shown in figure 1. Sensitivity, as slope of the calibration graph, results higher for the SAMT method that also shows a lower standard deviation on both slope and intercept as well as a better correlation coefficient. Anyway, these advantages are counterbalanced by a more complex procedure and the need of greater amount of sample; the last is obviously particularly important in the field of Cultural Heritage. For the SAMT method a good agreement resulted with an analogous curve obtained by other researchers[3] using the same enzyme but a different analytical technique.



A $y= (-2.7\cdot10^{-3}\pm0.4\cdot10^{-3})x+(10.4\pm0.7)$ $r^2=0.8868$; $t=8.77$; $(1-\alpha)=0.95$

B $y= (-6.8\cdot10^{-3}\pm0.7\cdot10^{-3})x+(13.5\pm1.0)$ $r^2=0.9222$; $t=14.37$; $(1-\alpha)=0.95$

Fig. 1; Calibration graphs obtained with dated linen samples by A) GOD method, B) SAMT method

Conclusions

In the case of the biosensor method an archeometric curve was recorded for archaeological textiles which can be used to evaluate unknown ages with a precision of about 90%.

This method is also faster, simpler and cheaper than the first, and can be used on smaller amounts of sample.

The SAMT method also resulted suitable to date ancient cellulosic materials. Even if for the archeometric curve reported in literature[3] a better confidence limit resulted, our determination of adenosine by GC-MS surely is more sensitive with respect to densitometric Tin Layer Chromatography with Ultraviolet detection (UTLC-UV) used in such previous research[3].

References

1) L. Campanella, F. Chicco, G. Favero, T. Gatta, M. Tomassetti, Further applications of a new biosensor method for dating cellulosic finds, *Ann. Chim.*, 95(3-4), (2005) 133-141
2) L. Campanella, G. Favero, F. Rodante, M. Tomassetti, S. Vecchio, Thermogravimetric and kinetic methods to date wood finds. First results, *Ann. Chim.*, 93(11), (2003) 897-907
3) D.A. Kouznetsov, A.A. Ivanov, P.R. Veletsky, Analysis of cellulose chemical modification: a potentially promising technique for characterizing cellulose archaeological textiles, *J. Archaeol. Sci.*, 23(1), (1996) 23-34