[Radiocarbon, Vol 25, No. 2, 1983, P 669-674]

POSSIBILITIES IN THE DATING OF WRITING MATERIALS AND TEXTILES

RICHARD BURLEIGH and A D BAYNES-COPE

Research Laboratory, The British Museum, London WC1B 3DG, England

This paper discusses the characteristics of the commoner classes of writing materials and textiles deriving from ancient and more recent historical sources and the problems they present for ^{14}C dating. The materials under consideration are, firstly, paper in various forms, parchment, and vellum (ancient papyrus, which poses different kinds of dating problems, is not considered) and secondly, fabrics such as linen, cotton, and woolen textiles, to which, from the dating point of view, similar technical considerations apply. Our main concern is with problems associated with the dating of paper.

The purpose of applying ^{14}C dating to paper (and parchment or vellum) will be to authenticate an archival document ("document" is used here to mean anything written, drawn, or painted on these materials, and "archival" to mean material bearing a date or datable by art-historical methods). Thus, much may depend on the result of any such ^{14}C measurement and an understanding of possible sources of error in the interpretation of the date obtained is of great importance.

Until recently, the relatively large amount of sample needed (ca 10g) has precluded the application of conventional ^{14}C measurement (by standard gas-proportional and liquid scintillation counting methods) to the dating of documents, as it has never been permissible to remove a sufficient quantity of material for worthwhile analysis. The same difficulty has sometimes arisen with ancient textiles, eg, two tunics from Tarkhan, Egypt (Burleigh, Matthews, and Ambers, 1982; Hall, 1982), with which individual garments have been too important to allow even partial destruction for dating (although without a precise date their archaeologic value may have been correspondingly diminished). With the advent of (in R L Otlet's terminology) "micro-" and "mini-" methods of ^{14}C measurement by means of accelerators (Hedges, 1981; Stuiver, 1978) and small counters (Harbottle, Sayre, and Stoenner, 1979; Otlet and Evans, 1982; Sayre et al, 1981), for which a few milligrams or less of sample are needed, the former constraint of minimum sample size has been removed. As a result, among many other important applications, the dating and authentication of a great diversity of hitherto imprecisely dated archaeologic finds and museum objects has become possible. In many, perhaps most, such instances, positive results will be obtained that will have real benefit to scholarship, but in some others the answers may be equivocal or even wrong. This risk applies particularly to the dating of paper documents and it is with the consequences of the inevitable application of the new methods to these (and not the technical aspects of the methods themselves) that this paper is chiefly concerned. The procedures suggested for the preparation of paper for dating (see Appendix) are appropriate also to textiles, although dates for textiles will not necessarily share the same sources of possible error. To explain the sources of systematic error to which ^{14}C dates for paper will be subject (apart, that is, from the random errors inherent in all ^{14}C measurements, and errors of the ^{14}C time scale itself), it is necessary to give a summary of the technological history of paper manufacture.

Until the early 1840s, paper was made from shredded and pulped cellulose rags (cotton and linen). These were indiscriminately collected and may have been of any age, perhaps commonly up to 100 years old, but the use of mummy wrappings from Ancient Egypt for paper manufacture in the mid-19th century has also been recorded (Hunter, 1957). This is an extreme example, but it serves to illustrate the nature of the problem. After ca 1840 the use of rags for paper manufacture was superseded by the introduction first of mechanical and later of chemical wood pulp, although a limited amount of higher quality rag paper is still made today for specialized uses. Wood pulp averages the age of the (de-barked) trees from which it is manufactured and again probably incorporates material representing up to 100 years or more of growth. Esparto (grass) papers, although in principle "annual," may also incorporate wood fibers. The practice of re-pulping paper, although known from China as early as ca AD 1380, was not in use in Europe before 1800. Thus, it is evident that any apparent age obtained for paper will antedate its manufacture and use, sometimes by a large margin (also, paper may have been stored for a considerable period before use). From this it is clear that the only valid ^{14}C date for a paper document will be one that is significantly older than its purported historical date. Even so, this will not always be sufficient proof of the authenticity of that document which must ultimately rest upon independent evidence such as handwriting (Harrison, 1958), although it may indicate that it is contemporaneous, or at the very least not inconsistent with, the age expected on historical grounds. By contrast, parchment and vellum were made from the skins of young animals (sheep or goat and calf, respectively), generally used soon after manufacture, and therefore, can be expected to have much smaller, usually negligible, apparent ages. Nevertheless, long after first use, parchment and vellum were often cleaned to remove the original ink and re-used, such documents being known as palimpsests. Similarly, although the basic textiles of antiquity - linen, wool, and silk - were probably manufactured from the products of a single season's growth more or less immediately after harvesting, re-use, in particular of wool for the manufacture of felt, is to be considered. A date for a textile provides essentially a *terminus post quem* as the period of time over which it was in use may remain indeterminate, while it is the date of the making of a document, the single event of the use of the paper, that is principally of interest, which may differ widely from the apparent ^{14}C age of the paper.

Finally, as a result of natural ^{14}C variations over the last few hundred years, a single measured ^{14}C age may correspond ambiguously to more than one alternative calendar date (Stuiver, 1982).

In view of these problems and the abundant historical documentation of almost all aspects of paper manufacture and technology, it is essential that a detailed technical examination of any document should be carried out before it is subjected to ^{14}C dating. If ^{14}C dating is to be used for this purpose at all it should be applied with a reluctance amounting to last resort. From an essentially non-destrictive preliminary examination of a paper document, such highly diagnostic features as the kind of fibers of which it is composed and their mode of preparation, the presence of specific chemical substances (eg, aluminum sulphate in modern papers), the nature of the size used, the use of "wove" or "laid" paper, the spacing of laid lines, the ink, and above all, watermarks, can all be determined (the last by beta-radiography, a mandatory procedure). A combination of the information obtained in this way may provide very precise historical dating as well as an indication of provenance, although it should be noted that, strictly, it is the application of the ink alone that dates the document. It would be difficult to obtain an adequate sample of the ink itself for ^{14}C dating and to add to this difficulty, ink may sometimes contain dead carbon. In contrast, therefore, to the precise information that will most probably be obtained from detailed technical examination of a document, it is unlikely that its age can be resolved satisfactorily by the application of ^{14}C dating, the results of which are more likely to provide confirmation of known trade practices in the manufacture and use of paper than an exact date (disregarding the additional problem of the ambiguities in the recent ^{14}C time scale). An example of the kind of "corroborative" application that might, however, be worth attempting is the dating of printed documents bearing, say, 16th or 17th century dates (and often of great value today if genuine), but on paper with unrecorded watermarks believed to be much later, perhaps 18th century date, implying later discovery and re-use of the original printing blocks (Baynes-Cope, 1981; Burleigh, 1981). The parchment of the Vinland Map, on the other hand, would probably not be datable as it is almost certainly a palimpsest made using ink that analysis has shown to be of 20th century origin (Baynes-Cope, 1974; McCrone and McCrone, 1974).

In summary and in conclusion, the only unequivocal application of radiocarbon dating to documents appears to be for invalidation purposes, where a document purporting to be much earlier was actually made from material incorporating artificial ^{14}C derived from thermonuclear weapon tests, in which the characteristic bomb-carbon signal can be observed. The dating of textiles by the new micro- and mini-methods of ^{14}C measurement appears much less problematic and, within the limits of resolution of the radiocarbon time scale, reliable results for these materials should be obtainable.

APPENDIX. Chemical pretreatment of paper and textiles before radiocarbon dating

The purpose of the pretreatment of paper and textiles is to isolate the original cellulose or protein, removing altogether other substances that may have been added during manufacture and which may contain carbon. For paper, these may include glue (or rosin), size, starch, casein, chalk, oils, gums and resins, and coloring such as Prussian blue, ultramarine, or indigo. Of these, generally only dyes were added to textiles (procedures for pretreatment of textiles have already been proposed by Elmore et al, 1981, and by Harbottle, Stoenner, and Sayre, 1981, with particular reference to the Turin Shroud). Preliminary standard tests should be made for evidence of heavy sizing (cold water does not wet paper), the presence of starch (addition of 0.1% iodine solution gives blue color), resins (drop of alcohol/chloroform produces ring), and for blue papers, Prussian blue (slowly turned brown by a drop of 10% NaOH), ultramarine (fades quickly with addition of 10% HCl), indigo (unchanged by solutions of acid or alkali). A generalized procedure that will remove all of these added substances from paper (and textiles) without destroying cellulose or protein fibers, simultaneously removing extraneous organic and other contaminants, and give a clean sample containing up to approximately 40% by weight of carbon ready for conversion to elemental carbon or CO_2 for ^{14}C measurement, is as follows: soak in cold, de-ionized water for 1 hour (use preliminary protease digestion if paper proves unwettable); boil for 1 hour in water; boil in 5% NaOH to disintegrate material into separate fibers, centrifuge, rinse with hot water; add 5% HCI (break up wad of fibers), warm, centrifuge, rinse to neutrality and dry ready for radiochemical conversion and final analysis. Additions or modifications to this procedure that may be needed are solvent extraction of persistent dyes, bleaching of persistent brown coloration with sodium chlorite/formaldehyde, and the substitution of dilute (5%) ammonia solution for NaOH, for the pretreatment of woolen textiles; silk that has disintegrated badly with age would be much more difficult to pretreat successfully and any such samples would need to be separately considered.

REFERENCES

Baynes-Cope, AD, 1974, The scientific examination of the Vinland Map at the Research Laboratory of the British Museum, in The strange case of the Vinland Map (Symposium Royal Geog Soc, London, Feb 4, 1974, paper 7): Geog Jour, v 140, pt 2, p 208-211.

__________ 1981, The investigation of a group of globes: Imago Mundi, v 33, p 9-19.

Burleigh, Richard, 1981, Note on radiocarbon (dating) of the Ambassadors' Globe: Imago Mundi, v 33, p 20.

Burleigh, Richard, Matthews, Keith, and Ambers, Janet, 1982, British Museum natural radiocarbon measurements XIV: Radiocarbon, v 24, p 229-261.

Elmore, D, Gove, HE, Beukens, RP, Litherland, AE, Purser, KH, and Rubin, M, 1981, A method for dating the Shroud of Turin, in Sox, HD, 1981, The image on the Shroud - is the Turin Shroud a forgery?: London, Unwin, p 163-169.

Hall, RM, 1982, Garments in the Petrie Museum of Egyptian Archaeology: Jour Textile Hist and Conserv, v 13, pt 1, p 27-45.

Harbottle, G, Sayre, EV, and Stoenner, PW, 1979, Carbon-14 dating of small samples by proportional counting: Science, v 206, p 683-685.

Harbottle, G, Stoenner, RW, and Sayre, EV, 1981, Procedure for the treatment of historical linen fabrics before carbon-14 dating, in Sox, HD, 1981, The image on the shroud - is the Turin Shroud a forgery?: London, Unwin, p 170.

Harrison, WR, 1958, Suspect documents, their scientific examination: London, Sweet & Maxwell, 583 p.

Hedges, REM, 1981, Radiocarbon dating with an accelerator-review and preview: Archaeometry, v 23, p 3-18.

Hunter, D, 1957, Papermaking, the history and technique of an ancient craft (2nd ed): London, Cresset Press, 611 p.

McCrone, WC and McCrone, LB, 1974, The Vinland Map ink, in The strange case of the Vinland Map (Symposium Royal Geog Soc, London, Feb 4, 1974, paper 8): Geog Jour, v 140, pt 2, p 212-214.

Otlet, RL and Evans, GV, in press, Progress in the application of miniature gas counters to radiocarbon dating of small samples in Mook, WG and Waterbolk, HT, eds, Internatl symposium on C-14 and archaeol, 1st, Proc: Groningen, PACT Jour, in press.

Sayre, EV, Harbottle, G, Stoenner, RW, Otlet, RL, and Evans, GV, 1981, Small gas proportional counters for the carbon-14 measurement of very small samples, in Methods of low-level counting and spectrometry: Vienna, IAEA, p 393-407.

Stuiver, Minze, 1978, Carbon-14 dating - a comparison of beta and ion counting: Science, v 202, p 881-883.

________ 1982, a high-precision calibration of the AD radiocarbon time scale: Radiocarbon, v 24, p 1-26.