A DRAFT PROTOCOL FOR THE C-14 DATING OF SHROUD SAMPLES BY PRETREATMENT FRACTIONS

OBJECTIVE – To investigate possible variations in the radiocarbon age of the Turin Shroud due to local contamination, exchange or anomaly.

HYPOTHESES TO BE TESTED

1. That the Shroud dates to the $13^{th}/14^{th}$ centuries
2. That the Shroud dates to an earlier period.

DATA TO CONFIRM HYPOTHESES

1. If hypothesis #1 is correct then all measurements on fractions and residual portions of the samples should fall within or after the $13^{th}/14^{th}$ centuries.
2. If hypothesis #2 is correct, then measurements on at least the residual portions of samples after intensive pre-treatment should be earlier than the 13^{th} century.

THE GENERAL PROBLEM – Extensive scientific examinations of the Shroud have yielded cumulative evidence that the image on the cloth is a genuine body imprint with the detailed pathology expected of a crucifixion victim. A date of 1^{st} to 5^{th} centuries was thus indicated for the cloth. Recent C-14 measurement on one small strip from the 22A yielded dates in the 13^{th} and 14^{th} centuries.

SCIENTIFIC PROBLEMS – The samples from the 22A cut are from an anomalous region, both regarding possible medieval restoration and the effects of the 1532 fire. The strip was removed from near a border added to the Shroud after its manufacture, at a point where this border veers outward. Medieval restoration, though unlikely, cannot be ruled out; measurement of another sample from elsewhere on the cloth would receive this.

More serious is the fact that the 22A sample is from a scorch area and water stain region. It was probably heated to above 300 °C and its radiocarbon content may have been altered by:

1) isotope exchange with substances possibly present in the cloth, e.g.

$$\underset{\text{(carboxyl)}}{CH_3CH_2OO_2Na} + \underset{\text{(sodium acetate)}}{CH_3{}^{14}CO_2Na}$$

$$\xrightarrow{300\ ^\circ C}$$

$$CH_3CH_2{}^{14}CO_2Na + CH_3OO_2Na$$

or with CO_2, CO or pyrolytic hydrocarbons released in the fire. (see note ** *[further below]*)

2) contaminants possibly present is the cloth at the time of the fire and dehydrated/degraded by the scorching, leaving residues locked in the cellulose structure and difficult to dislodge by ordinary pretreatment.

3) Chemical reactions with substances possibly contained in the water used to extinguish the smoldering cloth.

"Pristine" areas of the cloth (i.e., undamaged by the 1532 fire) may also have organic contaminants occluded in the cellulose structure, deriving from: 1) heavy handling and usage over the centuries, especially on the edges; 2) attachment at times to wooden boards, and since 1534 to a backing cloth, with subsequent exchange of degradation products; 3) "boiling in oil" of the relic mentioned in a 1502 text.

[note **: The detection and separation of carbon derived from isotope exchanges of the type cited above poses a special problem. The Shroud represents a very rare case in which the object to be dated has been involved in a fire long after its manufacture. A roughly comparable situation, that of a long-lived wood used in house beams in Akrotiri, gave ages generally 200-300 years later than the fire, for reasons as yet unexplained.]

SAMPLING STRATEGY – Two strips of 80mg and 60mg to be taken from "pristine" edge areas well clear of all scorch and water stain. The proposed sites (1D/E and 9B) should be checked against the 1978 data, especially uv florescence, for any indication of light scorch or other damage or influence (e.g. heavy deposition of pyrolysis products) from the 1532 fire.

One weft thread of 8 cm (4mg) to be taken from another pristine area in the main body of the cloth (16B proposed).

One sample of 100-150 mg to be taken from under one patch (19E proposed): 1978 radiographs should be consulted to determine which patch should be lifted for availability of material and other considerations.

Finally, a 150 mg sample of the backing cloth to be taken for an internal control.

SAMPLE SUMMARY

Location	Quantity	Condition	Comment
1D/E	80mg	pristine	upper right corner
8F	60mg	pristine	right edge
16B	4mg	pristine	main body
19E	100-150mg	charred	under patch
backing cloth	150mg	pristine	added in 1534

TECHNICAL SAMPLE DATA – No details are as yet available from the labs which dated the 22A samples. Sample size to weight ratio is estimated at 1 square centimeter to 20mg. Thread length to weight is estimated at 0.5mg per cm for weft threads. Carbon yield has been estimated at 20% to 50%, but this would depend to some extent on the manner and intensity of pretreatment techniques employed on the 22A samples.

GENERAL TESTING STRATEGY – Fractions will be obtained from both pristine and charred samples (except 16B), for measurement by AMS or CO_2 counting methods as appropriate. There will be no blinds or external controls: a sample from the backing cloth will serve as an internal control. Specific pretreatment methods will be applied to pristine and scorch/charred samples.

1) Pristine samples will be subjected to increasingly intense alkali or nitration pretreatment, with each sample separated into at least two fractions based on chemical/time gradients. The assumption is that any deeply occluded contaminging residues will go into solution before the most resistant portions of the cellulose.

2) Scorched/charred samples will be subjected to thermal/time gradients, to separate each sample into fractions based on any specific carbon release pattern observed, or otherwise on arbitrary collection units. The assumption is that any deeply occluded contaminating residues will go into solution before the most resistant portions of the cellulose.

SPECIFIC PRETREATMENT FOR EACH SAMPLE

<u>Pristine sample 1D/E 80mg:</u>
remove 10% (8mg) by standard pretreatment
remove another 20% (16mg) by NaOH wash – first fraction, to be measured by another AMS
remaining 40mg = third fraction, for CO_2 counting

<u>Pristine sample 9F 60 mg</u>:
remove 6mg by standard pretreatment
remove 12-18 mg by nitration – first fraction, for AMS
remove further 12-18 mg by nitration – second fraction, for AMS
remaining 18-30 mg – third fraction, for AMS

<u>Pristine sample 16B 4mg:</u>
standard pretreatment
measure by AMS

<u>Charred sample 19E >100mg</u>
remove 10 mg by standard pretreatment
collect carbon from early stages of firing – first fraction, for AMS
collect carbon from middle stages of firing – second fraction, for AMS or CO_2 counting
collect carbon from final stages of firing – third fraction, for AMS or CO_2 counting

<u>Backing cloth 150 mg:</u>
divide into 50 and 100 mg samples
treat according to standard pretreatment
measure by AMS and CO_2 counting

Naturally the details of each procedure would have to be determined in the laboratory, in response to the actual carbon yield and sample idiosyncracies.

RESPONSIBILITIES – The following is a suggested division of labor, subject to agreement of each party to be involved:

Collection of samples in Turin – all (if available)
Screening of samples – Adler, Otlet, Evin or Haas
Chemical fractions and Co2 counting – Otlet
Thermal fractions – Evin or Haas
AMS measurement – DuPlessy or Wolfli
Publication – all (drafting & editing – Meacham)

FUNDING – At this point there is no funding for the project and all participants should be prepared to draw on personal and/or institutional resources of time and equipment. Consideration may be given to seeking support from the National Science Foundation, Wenner-Gren Foundation for Anthropological Research, National Geographic, or other source of funding.

SCHEDULE – On the assumption that sampling may be permitted early in 1989, the measurement should be completed by August/September 1989 and the final report submitted for publication by the end of the year.

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