DUŠAN SRDOC — NADA HORVATINCIC

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RADIOCARBON DATING OF THE *LIBER LINTEUS ZAGRABIENSIS*

UDC 902.65:003.343.1:003.513.3 (497.13 Zagreb)

Original scientific paper

Radiocarbon. *dating of linen cloth fragments of the Zagreb mummy tvrappings toithout Etruscan inscriptions resulted in a mean Libby age equal to 2290 ± 48 years BP. Dendrochronological correction is fairly reliable for the period betvoeen 2200 and 2400 years BP tohich mode it* possible to *set the true calendric* ***age*** *at 390 ± 45 years BC. Our measurements confirm the age based on writing style obtained by F. Roncalli, who dated Liber linteus Zagrabiensis to the 3rd century BC. First century BC or AD are ruled out acoording to our measurements as alternative dates often quoted in literature. Besides the linen cloth, other datable materials assodated with the mummy were the embalming unguent and leaves. The unguent used in embalment procedure has unacceptably old radiocarbon age otoing to a CHCh soluble fraction, probably fossil resins and/or mineral oils, themselves much older. After extraction with CHCh, the insoluble residue consists of charred fragments of leaves and branches, pracHcaUy contemporaneous with the linen, as judged by its radiocarbon age. Leaves are also of the same radiocarbon age, however* ***the statistical*** *error has been much larger because of small quantity of available material. Various analyses or identifications of the associated material such as chemical microanalysis (C, H, S), IR and NMR measurements, pollen analysis and paleobotanical identification of leaves hod been mode possible through generous cooperation of many* ezperts *and institutions.*

1. Introduction

The dating of *Liber linteus Zagrabiensis,* the longest Etruscan inscription on linen, which found its way to Egypt to be used there as mummy wrappings, has until reoently been based solely on the style and mode of its lettering (Roncalli, 1980, 1980a). At least three different ages had been proposed: 3rd and lst century BC and lst century AD. The aim of this work was to determine the true age of linen cloth by applying radiocarbon dating method. Several fragments of linen wrappings without inscriptions, therefore of no considerable archaeological value, were used for dating. Besides linen cloth, other datable materials like unguent and leaves

were also dated. Prior to chemical processing of samples for radiocarbon dating, a series of analyses was done in order to investigate chemical composition of datable material. Also, a thorough search for potential contaminants which are harmful to radiocarbon dating was done. A parallel investigation of sample material was made possible through generous help by several scientists and their institutions. Organic microanalysis of soluble and insoluble fractions of the unguent was performed by Z. Sliepčević, while infrared spectroscopy of the soluble fraction of the unguent was done by M. Tomašević, both of INA, Zagreb. Pollen analysis was performed at Center for Scientific Research of the Slovene Academy of Sciences and Arts by A. Šercelj and M. Culiberg. Nuclear Magnetic Resonance (NMR) measurement was done by Z. Meić and X-ray fluorescence analysis was performed by M. Jakšić, both of Ruđer Bošković Institute. Samples of leaves and other botanical material were sent for identification to; Professor Dr Behre, Niedersachsische Landesinstitut fiir Marscheri und Wurtenforschung, Wilhelmshaven, FR Germany. Dr Paula Ruddal, Royal Botanic Gardens, Kew, Richmond, Surrey, England. Dr. I. Šugar and Mrs. Z. Lovašen, Dept. of Botany, Univ. of Zagreb.

2lExp<ftrimental procedure

2.1. Sample preparation

Fragments of linen cloth and leaves were inspected by binocular microscope to check for possible intrusion of extraneous material. For instance, a different weaving pattem would indicate a, piece of gauže used by M; Barić, the collector and donbr of the mummy, or by any other person ehgaged in possessing, transporting, storihg pr stutiying the,mvmmy and its wrappings, The microscopic inspection revealed a uniform texturey proving thus that we were dealing with the original material. HoWever,it also rišvealed traces of red and black paint on textile and brownish štairi dri leavesj The red. paint Was previpusly idehtified as mercury sulphide,]EgS(Kr.all, 1892) which is,very harmful to the gas counting process because it develops sulphur, dioxide during combustion of sample in oxygen. The carbon black was identified By the same aiith«r:as;»iv6iy black^, presumably charred ivory. It is very iikely tKat the ivory used in • piaking the Hack paint was somewhat older than the, textiles. Radiofearboh age :ofivoryis that of a median age of an elephant tusk, i. e. reflects the buildup of tusk material during an elephant's life. Ivory carbon black cannot be dissolved by any chemical procedure without destroying the textile at the same time. Fortunately, .the amount of ivory carbon black was negligible compared with the bulk of textile. In addition, during our standard chemical processing of textile samples, particles of carbon black were separated from linen threads and washed out. The chemically processed linen threads were snow — white and fluffy, without traces of red or black paint. Mercury sulphide was also either dissolved or separated from threads by boiling in 4% hydrocloric acid. To be on the saf e side, we cut of f and discarded parts of wrapings with visible red or black stains, prior to chemical processing.

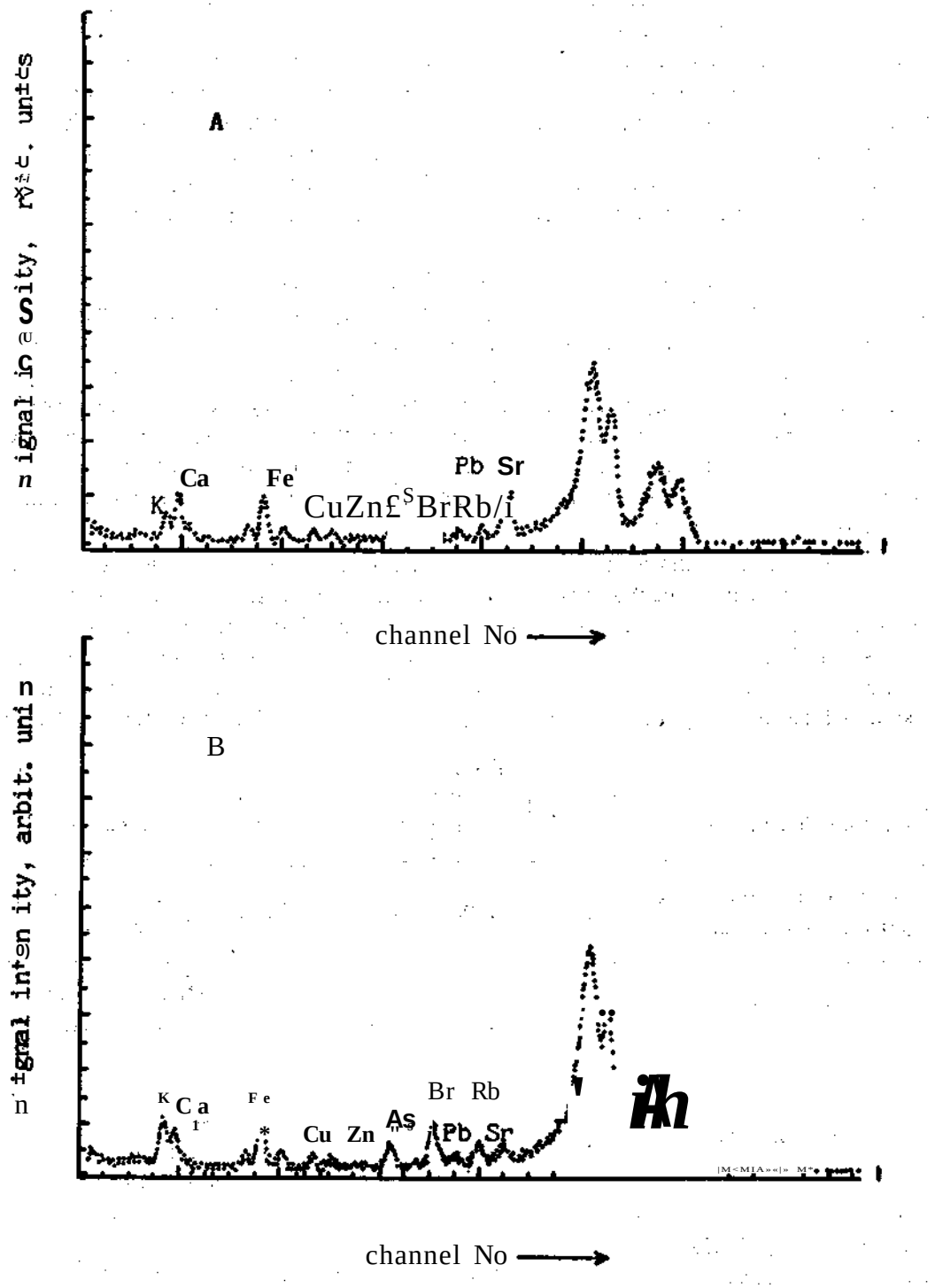

A
Ca
Fe
Pb Sr
K
CuZn£SBrRb/i
channel No
B
K Ca
Fe
Cu Zn
As
Br Rb
Pb Sr
channel No

Fig. a — SI. 1

Since the brownish stain on leaves was difficult to identify by microscope, we submitted both clean as well as stained leaves to x-ray fluorescence analysis. The results are shovm in Fig. 1. No paint containing heavy metals such as Pb or Hg or iron oxydes was used to dye the leaves, which were stitched to form, presumably, a wreath. We suppose that an organic dye was used to paint the leaves, which implies that no signif icant influence on radiocarbon dating could be attributed to the presence of an organic dye or stain. Namely, any dye prepared from leaves, flowers, seeds or fruits would have been practically contemporaneous with the textile.

The unguent was used in the embalming procedure to cover the body surface. Some pieces of the unguent reflect the body contours and contain textile patches embedded in the unguent surface. Some lumps have different structure from the rest of the unguent, having a shiny, asphalt-like consistence and a rounded shape, resembling solidified molten wax. Obviously, at a certain period of mummy storage or transportation, the whole structure was exposed to an elevated temperature, which had caused softening and a partial melting of asphalt or fossil resin used in embalming. The molten fraction oozed out of solid matrix, forming the described asphalt-like structures.

The original unguent is of dull grayish-black colour and very brittle. Upon extraction of CHCI3 soluble fraction in a Soxhlet apparatus the unguent disintegrated into small fragmente, less than 1—2 mm in diameter, which seem to be charred and crushed branches, leaves and seeds of various plants. According to literature (Dawson, 1929) the resins, balms and ethereal oils used in embalment are extracted from the plants which belong to the genera *Boswellia čarteri, Commip-*

Table 1.

Sample description	%C	%H	%S	% Ash	Comment
Original unguent; 4uH grayish-black lumps.	42.4	5.75	0.27	3.68	Brittle, linen cloth on the surface.
Fraction soluble in CHCI3	65.8	9.9	—	—	Extraction with CHCI3, Soxhlet extractor
Fraction insoluble in CHCI3	43.1	5.45	—	—	Residue, after extraction in Soxhlet extractor
Asphalt-like, CHCI3 soluble unguent samples	74.1	8.8	—	1.47	Shiny, rounded pieces of unguent

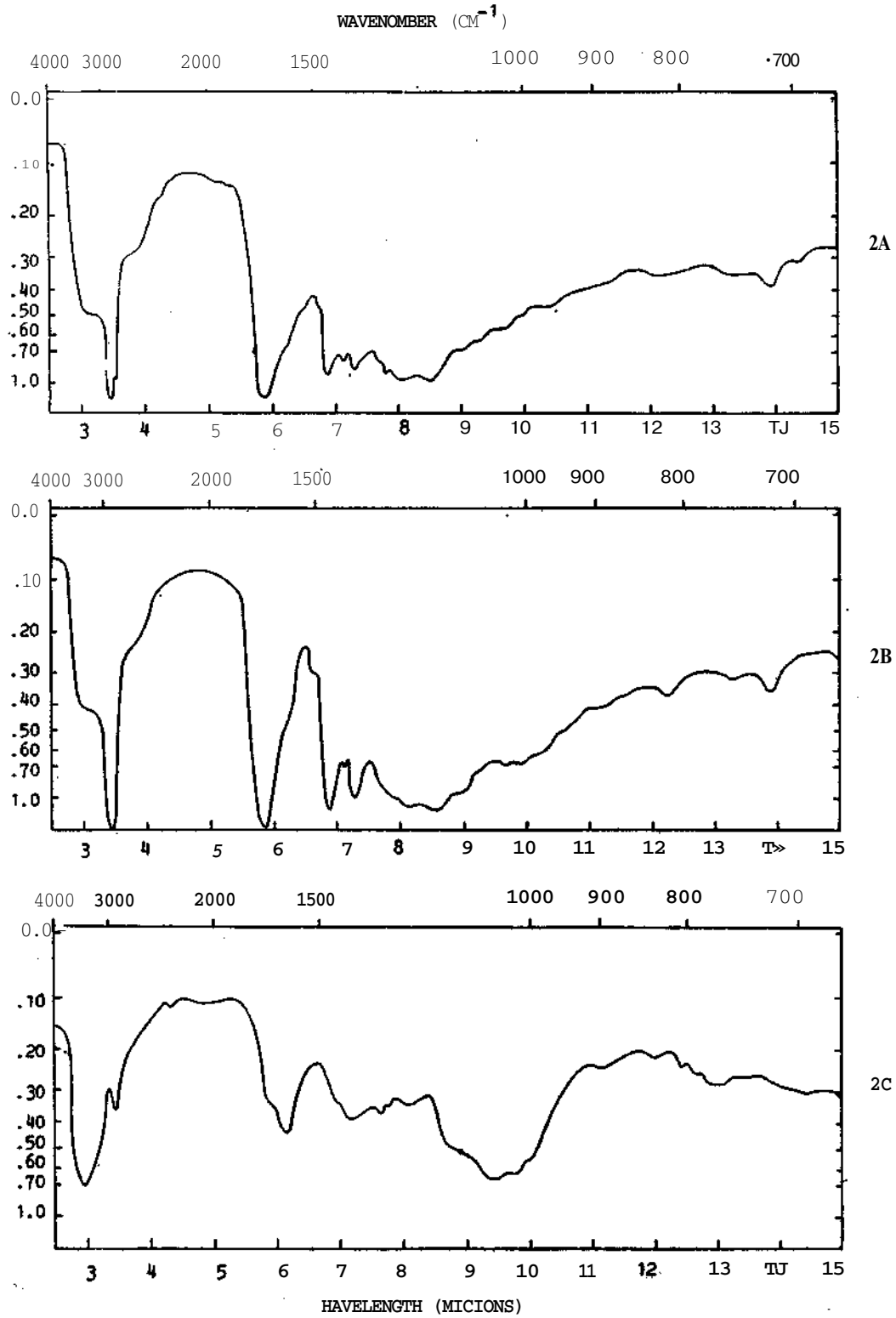


Fig. 2 (A, B,C) — SI. 2 (A, B, C)

hora abyssinica, Commiphora erythraea, Commiphora kataf, Commiphora opobalsamum, Cedrus libani, Pistacia lentiscus, etc. Ali these substances are convenient for radiocarbon dating, being practically contemporaneous with the mummy.

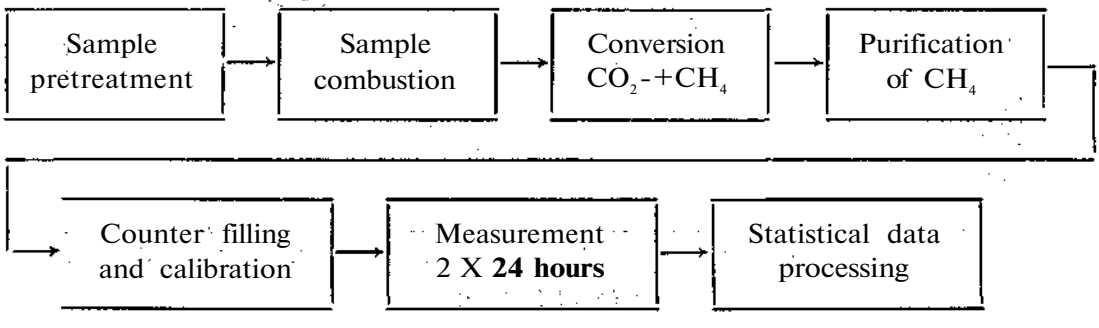
The results of chemical analyses performed by Z. Sliepčević, who used conventioinal and automatic microanalyzers are shown in Tab. 1.

Chemical analyses and solubility tests showed that at least two groups of components were used in making the tar-like, thick, brittle solidified unguent to be used in embalming. One group contains charred and crushed parts of various plants, insoluble in organic solvents, containing approx. 43^/0 of carbon. This component turned out to be very convenient and reliable for radiocarbon dating. The soluble components, on the other hand, contain a mixture of organic compounds, with much higher percentage of carbon, ranging from 66 to 74*Vo. The soluble and molten faction of the original material contain similar percentage of carbon and hydrogen.

The attempt to identify natural and/or fossil organic compounds by infra-red (IR) spectroscopy and nuclear magnetic resonance (NMR) resulted in several important findings, even though a complete identification of ali resins and oils used in the preparation of the unguent is beyond the resolving power of either instrument. Thus, IR spectroscopy confirmed our assumption that the asphalt-like substance, completely soluble in $CHCl_3$ exuded from the original unguent at elevated temperature. The IR spectra of the soluble and the exuded fraćtion of unguent shown in Fig. 2A and 2B are practically identical. The IR spectrum of the insoluble fraćtion, powdered and mixed with KBr shown in Fig. 2C represents mostly inorganic substances with characteristic groups OH and C-O-C. The IR spectra of soluble fractions in CHCI3 show the following functional groups: COOH and COOR. A comparison of spectra 2A and 2B with the IR spectra of natural resins of plant origin and of fossil resins indicate at similarity of aliphatic acid and esther groups in both cases. The abietic acid group indicates at derivatives of colophonium. The NMR spectra did not contribute to better understanding of organic constituents of the unguent.

2.2. Preparation ofsamples for radiocarbon dating

The samples of linen cloth, unguent and leaves were prepared for radiocarbon dating by the standard method used at the Ruđer Bošković Institute ^{U}C laboratory. The method is shown schematically on the block diagram:



The pretreatment of samples has been described earlier. The samples thus prepared are burnt following the method similar to elemental analysis in organic chemistry. Combustion is performed in a steady stream of oxygen purified from organic impurities by passing through silver wool heated at 750° C followed by the absorption of CO_2 on natron asbestos. Carbon dioxide is purified by passing over silver wool heated at 450° C. Nitrogen oxides are removed in an absorption tube filled with manganese dioxide.

Carbon dioxide is collected in traps and transferred into the reactor for conversion into methane. Carbon dioxide is converted to methane by the reaction with hydrogen, using ruthenium as catalyst. The reaction temperature is 470° C. Traces of water and carbon dioxide in methane are removed in the absorption tube filled with silicagel, natron asbestos and magnesium perchlorate. Samples are stored after combustion and conversion to methane for 14 days and then counted twice for approximately 24 hours each time in a proportional counter. Ali data on the sample, background and standard counting rates in 20 min. intervals, temperature and atmospheric pressure during measurements are statistically processed by HP 1000 computer.

Table 2

Sample description	No of measurements	Radiocarbon age ± 1 standard deviation (years BP). Libby half life of ^{14}C = 5568 yr.	Dendrochronologically corrected age; calendar years BC ± 1 standard deviation
Liber linteus Zagrabiensis. Linen wrappings of the mummy.	4	2290 ± 40	390 ± 45
Embalming unguent. Fraction insoluble in $CHCl_3$	3	2270 ± 40	380 ± 50
Leaves (Dicotyledon)	3	2380 ± 60	420 ± 80
Embalming unguent. Exuded fraction.	2	4540 ± 120	3350 ± 125
Embalming unguent. Fraction soluble in CHCl3	2	4590 ± 110	3380 ± 120

3. Results and discussion

3.1 Radiocarbon measurements

The pretreated and processed samples of linen cloth, leaves and embalming unguent have been repeatedly measured until the error inherent to radiocarbon dating approached its lowest value. The standard sample, (the oxalic acid distributed by the US National Bureau of Standards) as well as the background count rate measurements were alternated with the mummy samples. Results are shown in Tab. 2.

A comparison of radiocarbon ages of various materials reveals a sharp discrepancy in age between the linen cloth, the leaves and the insoluble fraction of the unguent on the one side and the exudated and extracted unguent on the other. The much older age of the soluble fraction of the embalming unguent tells us that one or several components used in the preparation of the unguent contained carbon that was much older than the rest of components, and that it was used in a chemical form which was soluble in organic solvents. There are two groups of organic materials, known to have been used in embalment belonging to that category: (1) Mineral oils, including asphalt (from Sinai shales?) and (2) fossil resins of plant origin. If mineral oils had been used, which do not contain any radiocarbon, it is possible to ćakulate (by using the radiocarbon measurements data), that the soluble fraction of the unguent contained approximately 25% of »dead« carbon, i.e. carbon in the form of mineral oil.

The linen cloth, the leaves and the insoluble part of the embalment unguent are of the same radiocarbon age, within -the statistical error of measurement. The very limited amount of leaves caused problems in ^{14}C measurement, hence the considerable error and deviation from the mean values of the linen and unguent age.

3.2. Dendrochronological correction of radiocarbon age.

The most important recent advancement in radiocarbon dating method is the application of so called dendrochronologic correction to the experimentally measured radiocarbon age. Namely, it has been realized that true calendric age differs from radiocarbon age of samples of known age for as much as 500 to 700 years in certain periods in the past. This phenomenon has been attributed to the small temporal variations of the cosmic ray flux, responsible for production of ^{14}C in the atmosphere. Fortunately, ali these variations are recorded in tree rings. A meticulous measurement of ^{14}C activity of individual tree rings of long living trees, such as the bristlecone pine in North America (lifespan: «s 7000 years) resulted in graphs and tables used for corrections of radiocarbon data (12th Nobel Symposium, Uppsala, 1970; 12th Radiocarbon Conference, Trondheim, 1985).

A typical calibration curve covering the period of time used for dendrochronological correction of our measurement is shown in Fig. 3. There are time periods which are very difficult to correct dendrochronologically; such is the period around 2500 years BP owing to rapid and erratic changes of the ^{14}C activity of the atmos-

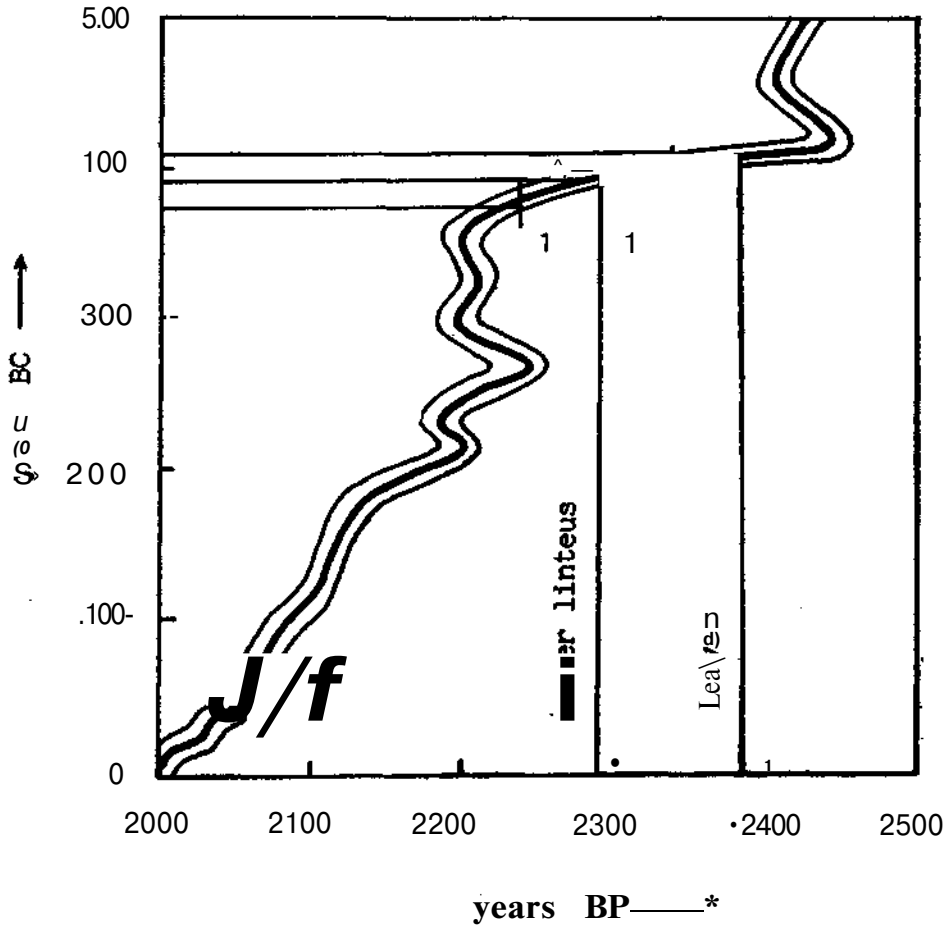


Fig. 3 — SI. 3

phere. Fortunately, the period of time between 2200 and 2400 years BP shows a very smooth and linear dependence of cialendric us radiocarbon time scale. Our mean value of the *Liber linteus Zagrabiensis* falls approximately in the middle of the linear section of the calibration curve (see Fig. 3) making possible to convert the radiocarbon age into true age of our sample fairly accurately. The dendrochronologically corrected values of our measurements of various materials associated with the Liber are listed in Tab. 2., last column.

Acknowledgments

We are grateful to ali individuals and institutions who generously contributed towards accomplishment of the work here presented. Ingrid Olsson of University of Uppsala gave valuable suggestion on dendrochronological corrections. Thanks are due to I. Mirnik and A. Rendić-Miočević of Archaeological Museum Zagreb for co-operation and to our colleagues B. Obelić and Ines Krajcar-Bronić for measurements and statistical processing of data. Elvira Hernaus meticuously prepared samples for radiocarbon dating.

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Figure Captions
Opis slika

Fig. 1. Trače element analysis of leaves by x-ray fluorescence method.
A-Leaves, unidentified species.
B- Leaves, same unidentified species, dyed or stained in reddish-brown color.
Both spektra show only traces of Fe, Cu and heavy elements (Pb, As).

Sl. 1. Analiza elemenata u tragovima pomoću rendgenske fluorescencije.
A — Lišće, nepoznata vrsta; B — Lišće, ista nepoznata vrsta, obojeno ili zamrljano crveno-smeđom bojom.
Oba spektra pokazuju teške elemente (Pb, As), zatim željezo i bakar u

Fig. 2. The infrared speetra of embalment-unguent,-2A/—Fractionof originalun-guent soluble in $CHQ1_3$; 2B— Exuded- unguent, tptally soluble in CH_3Cl_3; 2C — The insoluble fraction of the unguent. Residue after extraction of spr lublefraction with CHCl8, powdered,, mixedwith KBr and compressed.

Sl. 2. Infracrveni spektri smole upotrebljene pri balzamiranju.
2A Dio topive smole u kloroformu, CHCta.
2B Iscijeđena smola, topiva u CHCls.
2C Ostatak smole netopiv u CHCI3, zdrobljen u prašak, pomiješan s KBr i komprimiran.

Fig. 3. The calibration diagram to convert radiocarbon age into true age, bašed on dendrochronological measurements (after Pearson, in Proc. 12th Radio-carbon Conf., Trondheim, 1986.). The mean value of the radiocarbon age of the linen wrappings of the mummy *(Liber linteus Zagrabiensis)* ecjual to 2290 years BP corresponds to the midpoint equal to 390 years BC on the calibration curve. One standard deviation is shown on the BP scale.

S 1. 3. Kalibraciona krivulja za pretvorbu »radiokarbonske« starosti u kalendarsku starost (prema Pearson-u, Proc. 12th International Radiocarbon Conference, Trondheim, 1986). Srednjak radiokarbonske starosti lanenog povoja mumije Liber linteus Zagrabiensis (2290 godina prije sadašnjosti) odgovara 390 godini prije nove ere. Pogreška mjerenja (1 standardna devijacija) označena je na slici.

ODREĐIVANJE STAROSTI ZAGREBAČKE LANENE KNJIGE METODOM RADIOAKTIVNOG UGLJIKA

1. Uvod

Dosadašnje datiranje Zagrebačke lanene knjige, najdužeg etruščanskog napisa na lanenom platnu, upotrebljenom za ovoj egipatske mumije, izvršeno je jedino na osnovu stila i oblika njenog pisma (Roncalli, 1980, 1980a). Predložene su tri različite starosti: treće i prvo stoljeće p. n. e. i prvo stoljeće n. e. Gilj nam je da u ovom radu pomoću ^{14}C datiranja odredimo pravu starost lanenog platna. Za datiranje je upotrebijeno nekoliko fragmenata lanenog ovoja bez ikakvog natpisa. Osim lanenog platna datirani su uzorci smole i lišća koji su se nalazili uz mumiju. Prije kemijske obrade uzoraka, za radiokarbonsko datiranje napravljene su fizikalne i kemijske analize materijala. Posebno je bilo važno odrediti stupanj kontaminacije uzoraka zbog pogreške koja se time unosi u rezultate datiranja. Ispitivanje sastava uzoraka napravljeno je u nekoliko različitih institucija. U istraživačkom laboratoriju INA--GKI, Zagreb, Z.Sliepčević je izradio organsku analizu topive i netoprve frakcije, a topivu frakciju smole analizirao je M. Tbmašević infraervenom spektroskopijom. Polenske analize izradili su u Slovenskoj akademiji znanosti in umetriosti u Ljubljani A. Šereelj i M. Culiberg. Na. Institutu »Ruđer,Bošjković« Z.Meić je napravio mjerenja nuklearne magnetske rezonancije (NMR) smole a, analizu elemenata u tragovima fluorescentnim rendgenskim zračenjem napravio je M. Jakšić. Uzorci lišća i ostalog biološkog materijala poslani su na analizu u slijedeće institucije: Professor Dr Behre, Niedersachsiche Landesinstitut.fur Marschen und Wurtenforschung, Wilhelmshaven, FR Germany; Dr Paula Ruddal, Royal Botanic Gardens, Kew, Richmohd, Surrey, England; Dr I. Sugar i Ž. Lovašen, Prirodoslovno-matematički fakultet Sveučilišta li Zagrebu.

2. Eksperimentalni postupak

2.1. Priprema uzoraka

Uzorci lanenog platna i lišća detaljno su pregledani bindkularnim mikroskopom. Tim je postupkom provjereno da originalni materijal za datiranje ne sadrži strane primjese. Međutim, na tekstilu je primijećena crvena i crna boja, a na lišću smeđe mrlje. Crvena boja je već prije identificirana kao živin sulfid, HgS (Krali, 1892), koji je vrlo štetan kod kemijske pripreme uzorka za ^{14}C datiranje. Isti je autor

identificirao karbonsko crnilo kao »crnilo slonovače«, vjerojatno pougljenjena slonovača. Vrlo je vjerojatno da je pougljenjena slonovača starija od tekstila, pa bi se time unijela pogreška pri ^{14}C datiranju tekstila. Karbonsko crnilo slonovače ne može se otopiti niti jednim kemijskim postupkom koji ne bi istovremeno razorio i platno. Međutim, količina karbonskog crnila slonovače bila je zanemariva u odnosu na količinu tekstila. Cestice karbonskog crnila odvojene su i isprane standardnim kemijskim postupkom koji se primjenjuje u obradi uzoraka za datiranje. Kemijski obrađen uzorak tekstila bio je bijele boje, pahuljaste strukture, bez ikakvih tragova crne ili crvene boje. Živin sulfid je odvojen s tkanine kuhanjem uzoraka u 4% HCl. Dijelovi tkanine na kojima su bile vidljive crvene i crne mrlje, radi veće sigurnosti odrezani su i odvojeni od uzorka prije kemijske obrade. Smeđe mrlje na lišću bilo je teško identificirati mikroskopski, pa su ti uzorci analizirani fluorescentnim rendgenskim zračenjem. Rezultati su prikazani na slici 1. Analiza je pokazala da boja na lišću ne sadrži teške metale kao što su olovo, živa ili željezni oksid. Pretpostavljamo da su za bojenje lišća korištena organska bojila, čija prisutnost nema značajnijeg utjecaja na ^{14}C datiranje. Naime, bilo koje bojilo dobiveno od lišća, cvijeća, sjemenja ili voća bilo bi praktički iz istog vremenskog perioda kao i tkanina.

Smola je korištena u postupku balzamiranja za pokrivanje vanjske površine tijela. Na nekim dijelovima smole vide se konture tijela, a na površini smole ulijepljeni su komadi tkanine. Pojedini grumeni smole međusobno se razlikuju; neki su sjajnog izgleda kao asfalt i zaobljene forme, slični skrutnutom vosku. Očito je cijela, struktura bila izložena povišenoj temperaturi u određenom periodu pohranjivanja mumije ili prilikom transporta, što je prouzročilo mekšanje i djelomično taljenje smole.

Originalna smola je sivocrne boje, bez sjaja i vrlo krte strukture. Ekstrakcijom topive frakcije u Soxhlet-aparatu sa $CHCl_3$ smola se raspala u fragmente od 1 do 2 mm u promjeru, izgleda pougljenjenih i zdrobljenih grančica, lišća i sjemenja različitih biljaka. Prema literaturi (Dawson, 1929), biljna smola, balzam i eterična ulja koja se upotrebljavaju za balzamiranje ekstrahiraju se iz slijedećih biljaka: *Bostoellia čarteri, Commiphora abyssinica, Commiphora erythraea, Commiphora kataf, Commiphora opobalsamum, Cedrus libani, Pistacia lentiscus,* itd. Sve te tvari su pogodne za ^{14}C datiranje jer praktički pripadaju istom vremenskom periodu kao i mumija.

U Tabeli 1. prikazani su rezultati kemijskih analiza koje je Z. Sliepčević izradio na standardnom i automatskom mikroanalizatoru.

Kemijske analize i testovi otapanja pokazali su da su za postupak mumificiranja upotrebljene najmanje dvije grupe komponenata. Jedna grupa sadrži pougljenjene i usitnjene dijelove različitih biljaka, netopivih u organskim otapalima, koje sadrže približno 43% ugljika, što taj materijal čini vrlo pogodnim za ^{14}C datiranje. S druge strane, topive komponente sadrže smjesu organskih spojeva s mnogo većim

Tabela 1.

Opis uzorka	% C	% H	%>S	°/o Pe-peo	Komentar
Originalna smola, sivo-crni grumeni bez sjaja	42.4	5.75	0.27	3.68	Krhka smola; laneno platno na pòvršini
Frakcija topiva u $CHCl_3$	65.8	9.9	—	—	Ekstrakcija sa CHCI3, Soxhlet aparat
Frakcija netopiva U CHCI3	43.1	5.45	—	—	Ostatak nakon ekstrakcije u Soxhlet aparatu
Smola topiva u CHCI3 asfaltnog oblika	74.1	8.8	—	1.47	Sjajna smola, zaobljene forme

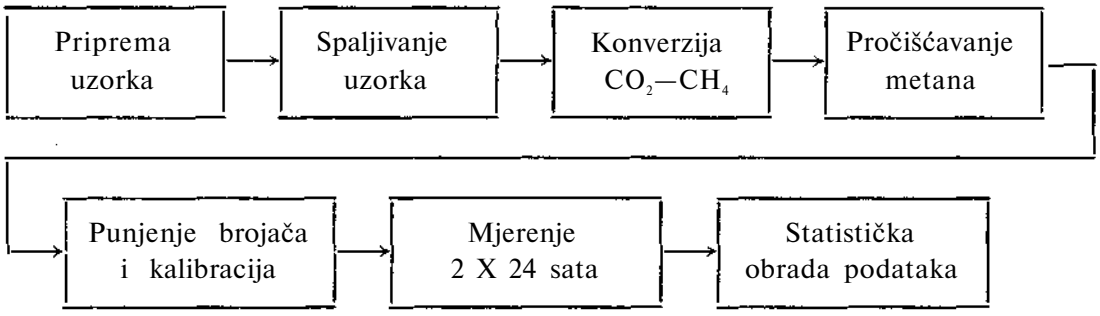
postotkom ugljika, od 66% do 74%. Topiva i rastaljena frakcija originalnog materijala sadrži sličan postotak ugljika i vodika.

Infracrvenom spektroskopijom i nuklearnom magnetskom rezonancijom dobivene su dodatne informacije o organskim spojevima u smoli, premda ni tim metodama nije bila moguća kompletna identifikacija svih biljnih smola i ulja upotrebljenih za preparaciju smole. IR-spektroskopija je potvrdila našu pretpostavku da se tvar asfaltnog izgleda, koja je kompletno topiva u CHCb, izdvojila iz originalne smole pri povišenoj temperaturi. Spektri topive i iscijeđene frakcije smole, prikazani na slici 2A i 2B, praktički su identični. IR-spektar netopive frakcije, usitnjene i pomiješane sa KBr, prikazan na slici 2C, predstavlja uglavnom anorganske tvari s karakterističnom grupom OH i C-O-C.

IR-spektar topive frakcije u CHCls pokazuje funkcionalne grupe COOH i COOR. Usporedba IR-spektra 2A i 2B sa IR-spektrima prirodnih smola biljnog porijekla i fosilnih biljnih smola pokazuje sličnost u alifatskim kiselinama i esterskim grupama u oba slučaja a posebno grupa abijetske kiseline indicira derivate kolofonija. NMR-spektar nije bitno pridonio daljnjim saznanjima u pogledu strukture organskih komponenata u smoli.

2.2. Obrada uzoraka za datiranje radioaktivnim ugljikom

Uzorci lanenog platna, smole i lišća pripremljeni su za ^{14}C datiranje standardnim metodama koje se koriste u ^{14}C laboratoriju Instituta »Ruđer Bošković«. Princip metode shematski se može prikazati na slijedeći način:



Priprema uzoraka je već prethodno opisana. Kemijski obrađen uzorak se spaljuje na način sličan elementarnoj analizi u organskoj kemiji. Spaljivanje se provodi u struji kisika pročišćenog od organskih onečišćenja, CO2 i vode. Dobiveni se ugljični dioksid pročišćuje prolaskom plina preko srebrne vune ugrijane na 450°C. Dušični se oksidi uklanjaju u apsorpcionoj cijevi punjenoj manganovim dioksidom. Ugljični se dioksid sakuplja u klopki i prebacuje u reaktor gdje se reakcijom s vodikom, uz prisutnost rutenija kao katalizatora, konvertira u metan. Temperatura reakcije je 470°C. Tragovi vode i ugljičnog dioksida iz metana uklanjaju se u apsorpcionoj cijevi punjenoj silikagelom, natron-azbestom i magnezijevim perkloratom. Pripremljeni uzorci u obliku metana spremaju se u metalne rezervoare i nakon 14 dana mjere u proporcionalnom brojaču. Uzorci se mjere dva puta po približno 24 sata. Svi izmjereni podaci — aktivnost uzorka, osnovnog zračenja i standarda u 20-minutnom intervalu, temperatura i atmosferski tlak za vrijeme mjerenja — statistički se obrađuju na računskom stroju HP 1000.

3. Rezultati i diskusija

3.1. Mjerenje starosti metodom radioaktivnog ugljika ^{14}C.

Pripremljeni i obrađeni uzorci lanenog platna, lišća i smole mjereni **su** nekoliko puta, dok pogreška mjerenja nije postigla najnižu vrijednost. Standardni uzorak, oksalna kiselina iz US National Bureau of Standards, kao i osnovno zračenje uređaja mjereni su naizmjenično s uzorcima platna, smole i lišća. Rezultati mjerenja prikazani su u Tabeli 2.

Usporedba ^{14}C starosti različitih materijala pokazuje izrazito neslaganje u starosti između lanenog platna, lišća i netopive frakcije smole s jedne strane, i iscijeđene i ekstrahirane smole, s druge strane. Mnogo veća starost topive frakcije smole pokazuje da jedna ili nekoliko komponenata upotrebljenih kod pripremanja smole sadrži ugljik koji je mnogo stariji od ostalih komponenata. Toj kategoriji pripadaju dvije grupe organskih materijala koji su upotrebljavani u postupku mumificiranja: (1) Mineralna ulja, uključujući asfalt (iz sinajskih škriljevaca?) i (2) fosilne smole biljnog porijekla. Ako su upotrebljena mineralna ulja, koja ne sadrže radioaktivni ugljik, moguće je izračunati (na osnovu izmjerenih podataka o sadržaju ^{14}C u uzorcima) da topiva frakcija smole sadrži približno 25% »mrtvog« ugljika, u obliku mineralnog ulja.

Tabla 2

Opis uzorka	Broj mjerenja uzorka	^{14}C starost uzorka ± 1 standardna devijacija Poluvrijeme raspada ^{14}C = 5568 godina (Libby)	Dendrokronološki korigirana starost i 1 standardna devijacija (godina prije nove ere)
Liber linteus Zagrabiensis, Laneni povoj mumije	4	2290 ± 40	390 ± 45
Balzam, netopivi dio smole u $CHC1_3$	3	2270 ± 40	380 ± 50
Lišće (Dikotiledon)	3	2380 ± 60	420 ± 80
Balzam, iscijeđena frakcija	2	4540 ± 120	3350 ± 125
Balzam, topivi dio u CHCI3	2	4590 ± 110	3380 ±120

Laneno platno, lišće i netopivi dio smole od mumificiranja imaju istu ^{14}C starost unutar statističke pogreške mjerenja. Veća pogreška i devijacija pri mjerenju starosti lišća u odnosu na srednju vrijednost starosti lana i smole prouzročena je vrlo malom količinom uzorka lišća za mjerenje.

3.2. Dendrokronološka korekcija ^{14}C starosti

U novije vrijeme često se primjenjuje tzv. dendrokronološka korekcija eksperimentalno izmjerene ^{14}C starosti. Naime, uočeno je da se prava kalendarska starost razlikuje od ^{14}C starosti uzorka za 500 do 700 godina u određenim periodima u prošlosti. Taj fenomen pripisuje se malim vremenskim varijacijama fluksa kozmičkih zraka, koje su odgovorne za produkciju ^{U}C u atmosferi. Srećom, sve te promjene zabilježene su u godovima drveća. Preciznim mjerenjem ^{14}C aktivnosti pojedinačnih godova vrlo starog drveća, kao što je tzv. »bristlecone« bor u Sjevernoj Americi (?» 7000 godina starosti), dobiveni su dijagrami i tabele koji se koriste za korekciju ^{14}C podataka (12th Nobel Symposium, Uppsala, 1970; 12th Radiocarbon Conference, Trondheim, 1985).

Na slici 3 prikazana je kalibraciona krivulja za vremenski period koji je korišten za dendrokronološku korekciju naših mjerenja. Postoji vremenski period koji je vrlo teško dendrokronološki korigirati, primjerice period oko 2500 godina prije sadašnjosti, zbog nagle promjene ^{14}C aktivnosti atmosfere. Srećom, vremenski period između 2200 i 2400 godina pokazuje vrlo laganu i linearnu ovisnost kalendarskog vremena o ^{14}C vremenskoj skali. Srednja vrijednost starosti Zagrebačke knjige nalazi se približno u sredini linearnog dijela kalibracione krivulje (vidi sliku 3) što nam omogućuje prilično točnu korekciju ^{14}C starosti uzorka. Izmjerene i dendrokronološki korigirane starosti različitih materijala vezanih uz Liber linteus Zagrabiensis prikazani su u Tabeli 2, posljednja kolona.

Zahvaljujemo se svim stručnjacima i njihovim matičnim institucijama u pomoći pri radu. Posebno zahvaljujemo Ingrid Olsson s univerziteta u Uppsali koja nam je pomogla pri dendrokronološkim korekcijama. Kolegama I. Mimiku i A. Rendić-Miočeviću zahvaljujemo na suradnji a B. Obeliću i Ines Krajcar-Bronić na pomoći u mjerenjima i statističkoj obradi podataka. Elvira Hernaus je vrlo pažljivo priredila sve uzorke, na čemu smo joj vrlo zahvalni.