ALTERNATIVE METHODS FOR CELLULOSE PREPARATION FOR AMS MEASUREMENT

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ABSTRACT. The main methods applied to clean plant material for radiocarbon dating are not compound-specific and generally remove only the easily exchangeable components by an acid-base-acid sequence and additional optional steps like Soxhlet extraction to remove resins and oxidative bleaching with $NaClO_2$. The products are normally clean enough for standard ^{14}C measurement, but in some cases it is desirable to have pure cellulose, which remains unchanged and immobile over longer time ranges, better representing the original plant material. In this work, 2 more compound-specific but still simple methods were tested to separate the cellulose from wood. The viscose method is based on the xanthification process used in the textile industry, where the alkali-cellulose with CS_2 forms a soluble cellulose xanthate, which is then extracted and cellulose is recovered. The second procedure is based on the wood/cellulose dissolution in ionic liquid 1-butyl-3-methylimidazolium chloride [BMIM]Cl, when the dissolved cellulose could be precipitated again by simply adding a water-acetone mixture. This process was recently reported, but still not used in sample preparation procedures for ^{14}C dating.

INTRODUCTION

Radiocarbon dating of various types of wooden artifacts and tree-ring sequences is applied very often and has played an important role since the ^{14}C method was established. The chemically stable components of wood are ideal to preserve the original carbon isotopes ratios and thus the age information. For a correct and reliable ^{14}C dating, it is necessary to take only that part of the material for which isotope ratios were not changed in the time between wood formation and measurement. Hence, in the sample preparation and treatment procedures all the mobile and isotopic ratio changing components should be removed.

The main components of wood are cellulose (40–60%), lignin (16–33%), hemicelluloses, and minor easily extractive components (5–10%) like resins, waxes, etc. The relative ratios of the components depend on the tree and wood type (Miller 1999; Walker 2006). Lignin is a 3-dimensional phenylpropanol polymer that binds the plant cells together in a mechanically and chemically stable network. Cellulose, the main wood component, is a linear polymer consisting of β-D glucose units. In the cell walls, it appears mostly in crystalline form.

For ^{14}C dating, preferably only the most stable part of the wood is used. This stable part is often defined as holocellulose, obtained after acid-base cleaning and bleaching with sodium chlorite (Leavitt and Danzer 1993; Gaudinski et al. 2005; Anchukaitis et al. 2008). The holocellulose can again be divided into an α-cellulose fraction, which is not soluble in 17.5% NaOH, and the soluble low-weight polymer fraction with variable composition is called hemicellulose. The α-cellulose is a long and very stable polymer. Thus, it stays unchanged and immobile over long time ranges, representing the isotopic composition of the original plant material, while lignins and hemicelluloses are considered to potentially change over longer terms.

To release the cellulose from wood and purify it, the lignin network has to be fragmented first and removed together with other plant components. Standard acid-base-acid methods very often remove only the easily exchangeable components; hence, they are not compound-specific, as desired in many cases. For better and more compound-specific separation, the Jayme-Wise or Brendel meth-

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ods and their modifications are widely used (Leavitt and Danzer 1993; Loader et al. 1997; Brendel et al. 2000; Gaudinski et al. 2005).

Cellulose dissolution in ionic liquids (IL) was intensively studied in recent years and is described in the literature (Swatloski et al. 2002; Remsing et al. 2006; Novoselov et al. 2007; Cuissinat et al. 2008b; Kosan et al. 2008) as a promising technique. The presented results show that 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) is an efficient cellulose solvents and could be used also for wood dissolution (Fort et al. 2007; Kilpeläinen et al. 2007) as an alternative for classical (not environment friendly) paper and textile industry processes and similar techniques, a medium for preparation of cellulose and its derivatives, or even ^{13}C analysis. The advantages of IL are low vapor tension, the possibility of their regeneration, and low aggressiveness, which allow improving cellulose treatment processes to higher technological level.

The viscose process is a standard well-known technique widely used for the commercial preparation of rayon. Cellulose, prepared from either wood pulp or cotton linters, is treated with sodium hydroxide and then with carbon disulfide, resulting in cellulose xanthate formation.

As far the authors know, these methods were not used in ^{14}C analysis to determine the ^{14}C age of wood or other samples. Hence, the aim of these experiments was to test the possibility of cellulose separation from wood in reasonable time with simple procedures and to test for possible contamination with carbon-containing compounds that have different isotopic composition and show the potential of these methods for ^{14}C dating of wooden compounds.

METHODS

IAEA C3 cellulose (129.41 ± 0.06 pMC, ETH 34908) was used as a reference material and brown coal (^{14}C-dead wood, ETH 34905) as a blank material for sample processing and accelerator mass spectrometry (AMS) measurements. The wood samples used in this study were obtained from Eichstätt (Germany). These 5-yr-blocks of dry oak wood came from tree cores No. 18 (ETH 37133–37164) and No. 9 (ETH 37165-37171) with a known calendar ages of AD 1111–1269 (No. 18) and 1271–1305 (No. 9). The Hoenggerberg oak wood (ETH 37129) was used as a supporting material to determine cellulose yields in preliminary tests. Only 1 large tree ring from 2001 was used. All wood samples were milled to fine powder by a hand driller with a small milling cutter (3-mm drill).

The yields of the methods were calculated from dry mass of the wood and the final cellulose. The IAEA C3 cellulose ^{14}C standard was used to determine the yield for cellulose. The washing steps at the end of the procedures were carried out at pH ~4. This pH protects the suspension against atmospheric CO_2 dissolution before the drying step.

Cellulose samples were graphitized on the AGE (Wacker et al. 2010a) and measured on the MICADAS system (Synal et al. 2007; Wacker et al. 2010b) at ETH Zurich to determine any possible contamination of the cellulose during the procedures.

BABAB

This base-acid-base-acid-bleaching (BABAB) method is a modified version of the widely used ABA method, extended with a bleaching step at the end (Gaudinski et al. 2005; Anchukaitis et al. 2008). The method represents the current standard cleaning procedure for wood. There are 2 main differences between the ABA and BABAB procedures. The first one uses the alkaline step at the beginning for the following reason. The alcoholic, phenolic, and carboxylic groups of the main wood components are more dissociated at high pH; thus, the wood structure is more disrupted than

in comparable acidic conditions. Partial or even full dissolution of wood compounds is efficiently used in the paper and textile industries, where the wood is treated in alkaline solutions first and cellulose is then more accessible for subsequent treatments. To achieve efficient "alkalization," the wood in BABAB was treated overnight in the hydroxide solution at a higher temperature (75 °C).

The second difference is the additional bleaching step after the ABA. Sodium chlorite is widely used in different variations for the bleaching. Often, acetic acid is added to buffer the solution at a pH of 3–5, where the chlorite oxidation is most efficient. Here, we used HCl in the oxidation step instead of acetic acid to avoid any possible acetylation (Anchukaitis et al. 2008). This allows simplifying the method as HCl is already used in the previous step. $NaClO_2$ is stable over some weeks in concentrated neutral or alkaline solutions. If a neutral $NaClO_2$ solution is used, it is possible to add an appropriate amount of $NaClO_2$ directly to the acid wood suspension resulting after the acid step and refill with water to a desired concentration. The resulting acid will set the pH to a weak acid region. For faster oxidation, it is possible to add 1–2 drops of 4% HCl to 10 mL of $NaClO_2$ solution.

Before adding the next chemical, H_2O washing steps were always added to raise the pH higher than 4 after each acid step, then to lower than 10 after a base step. The remaining concentrations of HCl or NaOH are negligible and do not influence the separation process. In the final washing step, the pH was brought to ~4 to avoid sorption of atmospheric CO_2.

The BABAB procedure is described in Figure 1. The whole procedure except the ultrasonic bath step was carried at 75 °C:

1. The wood (20–30 mg) was first washed in 5 mL of 4% NaOH overnight.
2. The solution was then removed and wood washed in 10 mL of ultrapure water and treated with 5 mL of 4% HCl for 1 hr.
3. The previous step was repeated with 4% NaOH instead of HCl.
4. Step 2 was repeated.
5. The solution was removed, then 5 mL of 10% $NaClO_2$, 5 mL of ultrapure water, and 2 drops of 4% HCl were added to the wood suspension.
6. After 2 hr of bleaching, the tubes were placed in an ultrasonic bath (25 °C) for 15 min.
7. The sharp yellow suspension (color caused by the formation of ClO_2) was separated and wood washed with ultrapure water to pH ~4.
8. The final product was dried in a standard laboratory oven overnight.
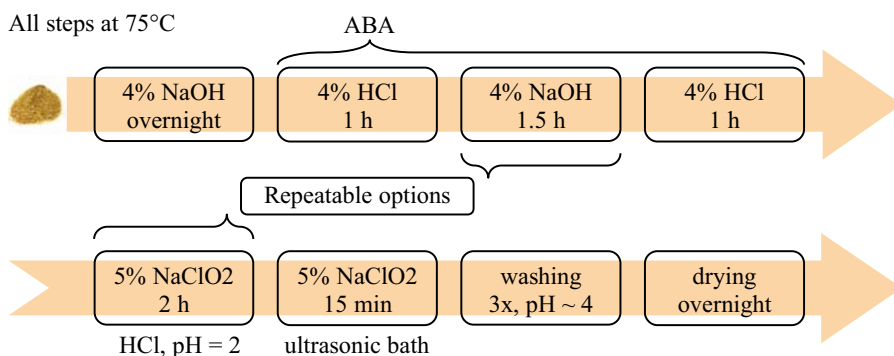

Figure 1 Simplified operational scheme of the BABAB procedure

Steps 2–4 represent a short ABA procedure; in our experiments, the longer ABA treatment was used, where each step lasts for 8 hr and wood was treated with 0.5M HCl and 0.1M NaOH at 60 °C.

Viscose

In the industrial process, the crushed wood (wood chips) are treated with the Kraft process, for example, where the wood is boiled at 140–180 °C at high pressure in the cooking liquor (basically a mixture of NaOH + Na$_2$S). During this pulping process, delignification takes place, and lignin and hemicelluloses are degraded to strong alkali soluble fragments. The resulting cellulosic material (brownstock) still contains up to 5% residual lignin, which is then removed in the following bleaching step. To produce cellulose rayon fibers in the viscose process, the purified cellulose is treated with NaOH, when cellulose reacts with NaOH to form alkali-cellulose:

$$cel\text{-}OH + NaOH \rightarrow cel\text{-}ONa + H_2O$$
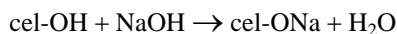
The alkali-cellulose is then incubated in 17% NaOH at 20 or 70 °C for several hours, where depolymerization takes place; the cellulose chains are cut and the polymerization degree is decreased from about 2000 to 500–600 units. After incubation, the excess NaOH is removed and alkali-cellulose brought into contact with CS$_2$:

$$cel\text{-}ONa + CS_2 \rightarrow cel\text{-}O\text{-}CS\text{-}SNa$$
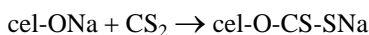
The formed yellow cellulose xanthate is dissolved in diluted (~4%) NaOH to form a yellow-brownish viscous solution called viscose. The more complete cellulose dissolution is then achieved during an additional 50–60 hr incubation at 16–20 °C in vacuum (ripening), where redistribution and loss of some xanthate groups takes place. After dilution, filtration, and deaeration, the dissolved cellulose is injected into a coagulation bath, which is often a mixture of H$_2$SO$_4$, Na$_2$SO$_4$, and ZnSO$_4$ at 40–55 °C. Under these conditions, viscose decomposes to alkali-cellulose and gaseous CS$_2$ (T$_b$ = 46.29 °C).

The final cellulose properties are influenced by NaOH concentration during the alkali/cellulose conversion and xanthification processes. The NaOH concentration also plays a role in the thiocarbonates formation, which then negatively influences the CS$_2$ consumption, quality, and yield of cellulose (Lazurina and Rogovin 1980). Moreover, insufficient decomposition of these carbonates can change the carbon isotopes ratios.

The proposed separation method proposed here is based on the industrial viscose process, modified for small samples and simple laboratory use and is described in following steps (see also Figure 2):

1. The wood powder (20–30 mg) was contacted with 5 mL of 17% NaOH overnight in 10-mL tube at 25 °C or 75 °C (Figure 3).
2. The solution was removed by 3 min centrifugation at 4000 RPM and wood was treated again with 5 mL of 17% NaOH solution for 1.75 hr. The NaOH solution was again refreshed and wood treatment continued for an additional 1 hr, all at 75 °C. All these alkaline steps should remove hemicelluloses, resins, and lignin and form the alkali-cellulose.
3. NaOH was then removed by centrifugation (4000 RPM, 3 min) and the wood suspension was contacted with 2 mL of CS$_2$ (purity ≥99%, Fluka) for 15 min in an ultrasonic bath.
4. Three mL of 4% NaOH were added to the tube mixture and the 3-layer system (Figure 4) was turned to emulsion by intense vortexing. Another 2 mL of NaOH were added after 2 hr. Emulsification was repeated several times during the 3 hr of total incubation time.
5. The orange xanthate solution was separated and injected into 10 mL of 10% (H$_2$SO$_4$ + Na$_2$SO$_4$) solution warmed to 75 °C. Xanthate was immediately decomposed, the CS$_2$ boiled out and its rests were removed in an ultrasonic bath.

6. The white precipitated cellulose was separated and washed again in 10% ($H_2SO_4 + Na_2SO_4$) solution.
7. A short bleaching step in 1% $NaClO_2$ at 75 °C for 15 min was used to remove any remaining non-cellulosic compounds.
8. The cellulose was again separated and washed with ultrapure water to pH ~4.
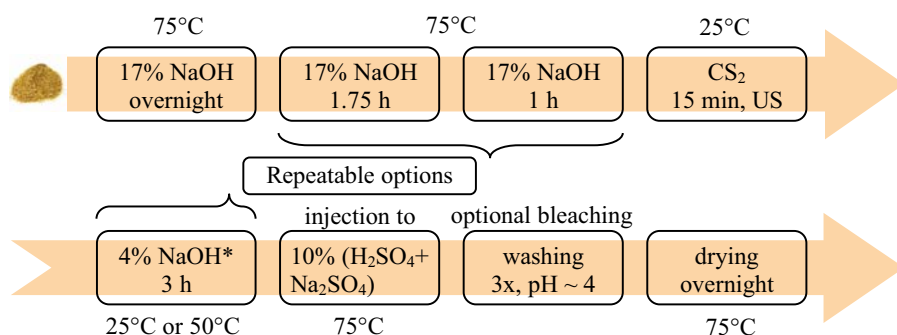9. Product was dried overnight at 75 °C.

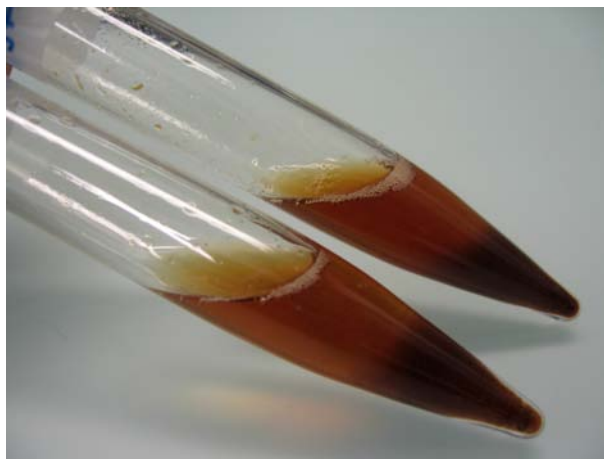Figure 2 Simplified operational scheme of the viscose procedure

Figure 3 Wood pulping in 17% NaOH; step 1 in viscose procedure.

Steps 4–9 were repeated several times in some cases to quantify the efficiency and additional parameters of the process. During the experiments, various temperature regimes were tested not only for wood treatment, but also for xanthate formation. In the first experiment (method A) with Hoenggerberg oak wood, a temperature of 75 °C was set in steps 1 and 2 and the xanthification ran in 12% NaOH at 25 °C (step 4). For the next cellulose extraction test, the concentration of NaOH was increased to 17% in step 4 and the xanthification ran overnight (method B). During this time, the CS_2 was consumed (thiocarbonates formation) and an additional 1 mL was added. Then, after viscose separation (step 5), the resulting wood material was treated with an additional extraction at the same conditions. Cellulose was precipitated at 45 °C.

In method C, the Eichstätt oak wood was treated at 25 °C in steps 1, 3, and 4, while in step 2, the wood was leached at 60 °C. Again, the extraction step was repeated after the viscose separation.

The last modification (method D) used 75 °C for Eichstätt oak wood leaching in NaOH in steps 1 and 2, but the xanthification temperature was increased to 60 °C, above the bowling point (46 °C) of CS_2. Boiling was avoided because the surface of the CS_2 phase was covered by upper wood and NaOH phases (see Figure 4).

Figure 4 Three-phase (from bottom to top: CS_2, wood, NaOH) system during the xanthification step.

Ionic Liquid

[BMIM]Cl (Zhang et al. 2005) is a white crystalline hygroscopic substance with very low vapor tension. It melts at $T_m = 73$ °C to form a viscous champagne-colored liquid and can be easily dissolved in various solvents (Domańska and Bogel-Łukasik 2004; Novoselov et al. 2007) and regenerated by salting-out after usage (Mikkola et al. 2007).

In our wood dissolution experiments, [BMIM]Cl from BASF production and purity >95% was used. The solubility of cellulose in [BMIM]Cl is about 8 wt%; this means the ionic liquid (IL)-cellulose ratio should be higher than 12.5. Here, ratios of 15–27 for IL-wood were used. Additionally, additives like dimethylsulphoxide (DMSO, Fluka, purity >99.0% for GC) or polyethyleneglycol (PEG, Sigma-Aldrich, $M_{avg} = 200$) were used to decrease the high viscosity of the mixture.

The procedure is described as follows and shown in Figure 5:

1. The IL and the wood were dried at 110 °C overnight; this step was necessary because water content above 1% significantly suppress cellulose solubility (Cuissinat et al. 2008b).
2. After drying, the wood (20–30 mg) was added to melted [BMIM]Cl (25× excess) at 110 °C and immersed in IL by 3 min centrifugation at 4000 RPM. Later, the suspension was periodically stirred with a warmed stainless steel spoon for 6–7 hr.
3. DMSO or PEG was added to decrease the viscosity (see Table 2).
4. The undissolved part of the wood was removed and a 1:1 water-acetone mixture (WAC) was added to the liquid phase to precipitate cellulose.
5. The formed cellulose gel was washed once with 8 mL of WAC and twice with ultrapure water. The gel was then bleached for 10 min with 15 mL of 1% ($NaClO_2$ + HCl) and again washed with ultrapure water to pH ~4.
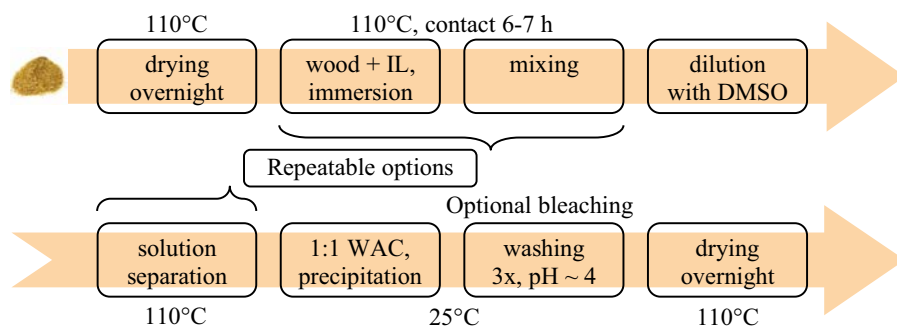6. The gel was dried overnight at 110 °C.

Figure 5 Simplified operational scheme of the ionic liquid procedure

RESULTS

The final product of the BABAB procedure is a white porous and chalky material, its texture still similar to the initial wood powder. The properties depend on the initial wood powder fineness and the intensity of the optional bleaching step. The yield of the BABAB procedure was $30 \pm 3\%$ for tree core No. 18 and $24 \pm 3\%$ for No. 9. The yield is mainly influenced by wood type, its preservation, and the efficiency of the separation step, where losses occur during decantation after centrifugation. As a processing blank, brown coal (ETH No. 34905) was treated with the BABAB procedure and its pMC value could not be distinguished from the graphitization blank.

The viscose procedure showed the possibility to separate cellulose from wood in a short procedure. Various temperature regimes and multiple extractions were used to see the influence on the cellulose yield (Table 1).

Table 1 Cellulose yields for the modifications A–D of the viscose method.

		Yield (%)		
Method	Sample type	Extraction 1	Extraction 2	Extraction 3
A	Hoenggerberg	11.1 ± 1.7		
B	Hoenggerberg	39.7	11.0	
C	Eichstätt	8.6 ± 2.3	6.8 ± 1.3	6.1 ± 2.1
D	Eichstätt	5.7 ± 1.0		
D	IAEA C3	47.5		

Table 2 Wood, ionic liquid (IL) amounts, and the yield for the IL procedure.

Sample[a] ETH-	GT nr	Wood (mg)	[BMIM]Cl (mg)	Ratio	Time (hr)	Solvent (mL)/ type	Cellulose (mg)	Yield (%)
37129	582	51.8	888.5	1:17	6	1/DMSO	9.824	19.0
37129	583	51.7	792.3	1:15	6	1/PEG	precipitation	
37129	564	40.3	640.7	1:16	3	2 PEG drops[b]	6.602	16.4
37129	584	51.5[c]	920.4	1:18	6	2/DMSO	1.441	2.8
37140	806	28.0	674.8	1:24	6	0.5/DMSO	4.768	17.0
37146	807	26.0	694.5	1:27	6	1/DMSO	3.554	13.7
37155	808	26.2	661.7	1:25	7	0.25/DMSO	3.219	12.3
37166	809	23.9	603.8	1:25	7	0.25/DMSO	3.051	12.8
C3	810	35.5	579.7	1:16	6	0.5/DMSO	26.48	74.6

[a]Hoenggerberg wood (ETH 37129), Eichstätt wood (ETH-37140 to -37166), and IAEA C3 cellulose.
[b]PEG was mixed with IL before wood addition.
[c]Wood was only cut to pieces ~1 mm in diameter.

The sequential extraction in method C yielded ~20% cellulose from the wood powder. A comparison of the cellulose yields in modifications A–D shows the presumed positive influence of higher temperature in the first leaching steps and the inhibition of temperature above CS_2 boiling point in the xanthification step. On the other hand, the difference could be influenced by cellulose accessibility in different and younger wood as well. The yield in B was significantly higher and thus shows the positive effect of 17% NaOH and increased temperatures during the pulping steps and time dependence of xanthate formation. But in this case, a significant part of CS_2 was consumed to thiocarbonates formation, which in B resulted in contamination and scattered results (119.22 ± 0.49 and 90.23 ± 0.41 pMC).

The cellulose yields in the viscose procedure can be explained again by the accessibility of the cellulose and its content in the wood, the efficiency of viscose production and its separation from residual wood particles, and again by decantation losses after centrifugation. Nevertheless, 47.5% of the cellulose was recovered from IAEA C3 cellulose in the least-efficient method (Table 1, method D), where the real content of α-cellulose is not known. These acceptable results might even be improved with a more advanced procedure in future. The final product of the viscose procedure is a hard compact material, similar to plastic.

The main problem with the ionic liquid (IL) procedure was the separation of melted [BMIM]Cl with the dissolved cellulose from the remaining wood particles. After contacting the IL with wood, the viscosity increased and it was difficult to stir the mixture; moreover, the stainless steel tools had to be warmed to 110 °C to minimize the losses of material on the tools. Separation of the remaining wood particles and the IL was carried out by centrifugation of the hot mixture. Due to its high viscosity, several shorter (up to 4 min) centrifugation steps were used and the mixture was heated again between steps.

After polyethyleneglycol (PEG) was added to the IL-wood mixture, the cellulose was immediately precipitated and even the [BMIM]Cl addition and longer heating did not dissolve the gel again. When the PEG was mixed with [BMIM]Cl before the wood addition, the powder particles started to swell. It was not possible to distinguish between swollen and dissolved material. The difficult separation resulted in a virtually higher yield because some swollen wood was taken as well.

An important observation was presented by Willauer et al. (2000); they demonstrated that lignins could be separated from cellulose with extraction from the salty-water phase to the PEG-2000 rich phase, where the cellulosic materials showed an absolute preference for the salt-rich phase in the polymer-based aqueous biphasic system. However, PEGs are supposed to support cellulose dissolution, but the dissolution may take place only at special conditions. For example, Yan and Gao (2008) found the chemical system PEG-NaOH is able to dissolve cellulose.

When dimethylsulphoxide (DMSO) is added, it is intended to act only as a diluting agent and to reduce the viscosity of the IL. The addition of DMSO at the end of the IL solvent step did not precipitate the cellulose and enhanced the separation. However, the wood was dissolving or swelling very slowly when it was initially added to [BMIM]Cl-DMSO mixture. This corresponds with observations (e.g. Cuissinat et al. 2008a,b; Fort et al. 2007) in which retardation of the cellulose dissolution in a similar mixture is reported. Only Kilpeläinen et al. (2007) reported good and rapid wood dissolution in a [BMIM]Cl-DMSO mixture. This could be explained by the disruption of swollen particles via intensive stirring.

The efficiency of the method is shown on the IAEA C3 cellulose sample, when 75% was recovered after full dissolution. IAEA C3 was dissolved very rapidly (Figure 6) and after 3 hr no residuals

were visible. The hot digestion of Eichstätt wood in [BMIM]Cl resulted in cellulose yields of $14 \pm 2\%$ (Table 2). A slightly higher yield was obtained for Hoenggerberg oak wood, which was also observed in the viscose procedure. Significantly lower yield (<3%) was obtained when the wood sample (584) was not drilled but only cut to small pieces (~1 mm in diameter). Thus, particle size plays an important role in wood dissolution and cellulose extraction.

Figure 6 Small piece of C_3 cellulose dissolving in pure [BMIM]Cl at 110 °C

Freshly precipitated cellulose was a slightly brownish hydrated gel (Figure 7C). The color was caused mainly by the residuals of IL and probably the remnants of some colorful compounds or fine fractions from the wood powder that were not sufficiently separated. The washed and bleached precipitated cellulose is no longer brownish (Figure 7D). Washing is an important step in removing all the colorful and IL residuals, mainly because IL is ^{14}C-dead and could potentially contaminate young wood. The color of the prepared dry material was not white in all cases, which could be due to the partial decomposition by the remnant bleaching agent and acid or still some remaining colorful compounds. The final product is a hard compact material, similar to plastic but with a slightly fibrous structure.
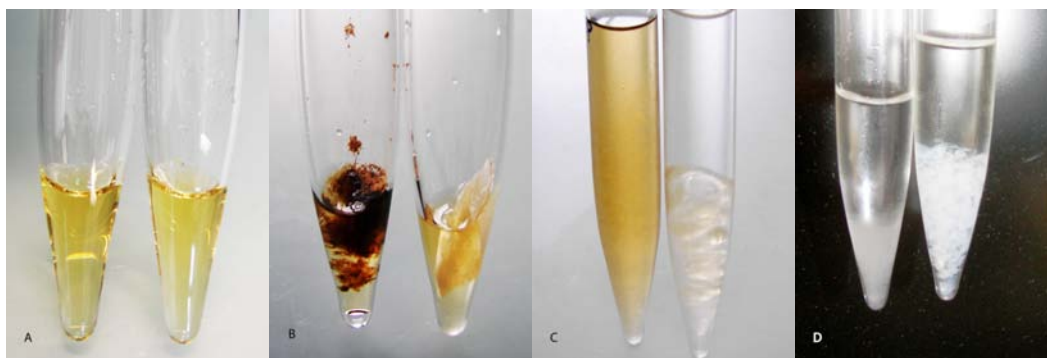

Figure 7 A) melted [BMIM]Cl; B) wood and cellulose contacted with IL; C) cellulosic material after precipitation but before washing; D) washed and bleached product.

Untreated Hoenggerberg oak wood (104.81 ± 0.15 pMC) and pure [BMIM]Cl (0.19 ± 0.03 pMC) were measured to quantify the possible contamination by "dead" carbon from the solvent in the first tests. The highest contamination was found in sample 583 (100.50 ± 0.27 pMC), resulting from precipitation of the wood-IL mixture after PEG addition and following insufficient washing. Samples 564 and 584, where no precipitation occurred and which were washed more carefully, showed good agreement with the original wood pMC value (104.07 ± 0.27 and 105.22 ± 0.26 pMC, respectively).

[14]C measurements of the IAEA C3 cellulose for ionic liquid (129.56 ± 0.16 pMC) and viscose (129.61 ± 0.14 pMC) are in very good agreement with the reference value (129.41 ± 0.06 pMC); no contamination with ^{14}C-dead material was found.

The ^{14}C results of Eichstätt wood samples are summarized Table 3 and Figure 8. The different methods produced ages that are in general good agreement with the IntCal04 curve (Reimer et al. 2004). The base-acid-base-acid-bleaching (BABAB) values are very consistent and reproducible, but show a significant offset of 26 yr to older values (Wacker et al. 2010b). The same is probably also true for the ionic liquid (IL) and the viscose procedure. The results from the IL method are in good agreement with the BABAB data, showing the same offset. The results of simple acid-base-acid (ABA) treatment are more scattered compared to the BABAB method but are in better agreement with the IntCal04 data set.

Table 3 Measured ^{14}C ages for samples treated with the different methods.

Sample	Average age (AD)	BABAB [BP]	ABA [BP]	Viscose [BP]	IL [BP]
37133	1113	967.5 ± 15.4	939.4 ± 14.4	1008.0 ± 20.1	
37134	1118	959.1 ± 15.0	940.2 ± 14.5	863.5 ± 18.8	
				988.3 ± 23.9	
37135	1123	955.4 ± 15.0	936.7 ± 14.5		
37136	1128	939.3 ± 15.1	978.0 ± 16.3		
37137	1133	954.0 ± 15.3	942.9 ± 14.5		
37140	1148	960.0 ± 14.3			965.9 ± 18.0
37141	1153	926.3 ± 15.1	923.5 ± 14.4	969.9 ± 19.4	
				972.6 ± 20.8	
37142	1158	927.2 ± 15.2	883.8 ± 14.7		
37143	1163	895.1 ± 14.8	850.5 ± 14.4	901.4 ± 19.1	
37144	1168	899.3 ± 14.3			
37145	1173	908.5 ± 15.0	890.5 ± 15.2	915.5 ± 18.6	
37146	1178	920.0 ± 14.2			902.6 ± 18.3
		945.0 ± 20.0			
37147	1183	917.5 ± 19.3		928.5 ± 19.1	
		867.7 ± 14.2			
37155	1223	869.3 ± 14.3			870.0 ± 17.8
		869.0 ± 18.3			
37156	1228	875.4 ± 14.3			
		876.6 ± 17.8			
37157	1233	834.7 ± 19.1			
		806.9 ± 14.1			
37158	1238	862.8 ± 14.4			
		849.3 ± 18.7			
37159	1243	819.4 ± 14.8		836.4 ± 18.8	
		818.0 ± 18.7			
37160	1248	837.1 ± 14.1		806.8 ± 19.5	
				819.9 ± 19.1	

Table 3 Measured ^{14}C ages for samples treated with the different methods. *(Continued)*

Sample	Average age (AD)	BABAB [BP]	ABA [BP]	Viscose [BP]	IL [BP]
37161	1253	820.5 ± 15.3	801.7 ± 15.2		
37162	1258	813.4 ± 17.0	810.7 ± 15.1		
37163	1263	790.1 ± 14.9	789.0 ± 15.9		
37166	1278	757.1 ± 14.1			748.6 ± 18.2
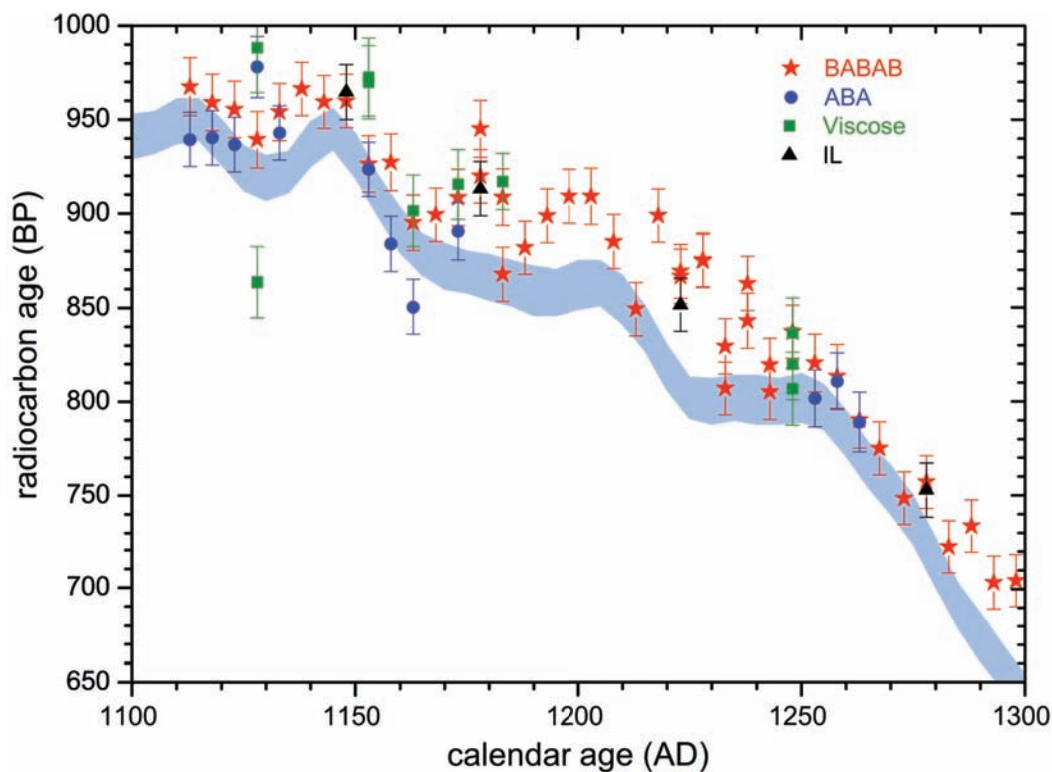
Figure 8 ^{14}C ages (BP) of Eichstätt wood samples prepared with different methods and compared to the IntCal04 calibration curve (Reimer et al. 2004).

Values obtained in repeated preparation with the viscose method correspond well within 1-σ uncertainties, but several outliers of both younger and older ages occurred. This cannot be easily explained by solvent contamination and we suspect other external contamination. Additional tests will be needed to get reliable results.

SUMMARY

The main purpose of these experiments was to develop and test alternative cellulose preparation procedures potentially suitable for AMS measurements. These alternatives are not meant to completely substitute standard ABA and bleaching methods, but to show an additional and applicable way to separate cellulose from wood and contaminants (e.g. for quality control).

The IAEA C3 cellulose was dissolved quickly with practically no remains in both the ionic liquid and viscose procedures. Hoenggerberg and Eichstätt wood were not fully dissolved, but a reasonable amount of cellulose was extracted in all cases. The tested methods vary in their compound specificity and hence it is only of minor relevance to compare directly their yields. Nevertheless, from the IAEA C3 cellulose standard, the α-cellulose yield for the viscose method was almost 50%, while the holocellulose yield for the ionic liquid method was 75%. For wood samples, the absolute yields were approximately 30% for BABAB, 10–20% for viscose, and 14% for IL.

These methods all gave satisfactory results, and the ^{14}C results in general fit very well to values obtained in the reference BABAB method.

From our first tests, we can draw the following conclusions:

- The higher specificity of the viscose and IL methods resulted in lower yields of cellulose extracted from wood compared to the BABAB and ABA procedures.
- Although the yields of the pure cellulose are already relatively high, they can still be improved by more careful phase separation and potentially by tuning the reaction conditions. The wood treatment before the cellulose separation should be improved to provide better cellulose accessibility for dissolution or xanthification.
- The ionic liquid should dissolve all the cellulosic compounds (Kilpeläinen et al. 2007). However, the dissolution of wood depends on its particle size and stirring of the IL/wood mixture, and the yield is strongly influenced by difficult separation of undissolved wood particles. The purity of the amorphous product depends on the efficiency of separation, precipitation, and washing.
- The ^{14}C ages of the prepared samples are in good agreement. Only in the viscose samples did some outliners occur.
- The pMC values of IAEA C3 treated with viscose or ionic liquid methods are in very good agreement with the reference value; no contamination of ^{14}C-dead material was observed.
- The ^{14}C age for the BABAB, viscose, and IL methods are consistent but slightly older than the IntCal04 calibration curve throughout the investigated time interval, while the simple ABA ^{14}C ages fit onto the curve or are even slightly younger.

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