

Comparison of the classical wood extraction method using a Soxhlet apparatus with an advanced extraction method

M. Schwanninger, B. Hinterstoisser

Extraction of wood meal is generally the first, very time consuming step during the wet chemical analysis of wood and wood components. Solvents like toluene, benzene, dichloromethane, ethanol, methanol and water with increasing polarity are used in accordance with standard methods using a Soxhlet apparatus. The comparison of the standard method with the advanced extraction method clearly showed that the lower solvent demand and the thoroughly removal of the solvent at the end of an extraction step increased the effectiveness of the following washing step. The time need for the determination of the extractives contents and the standard deviations of the repeated measurements could be halved.

Vergleich der klassischen Holzextraktionsmethode unter Verwendung einer Soxhletapparatur mit einer fortgeschritteneren Extraktionsmethode

Die Extraktion von Holzmehl ist im Allgemeinen der erste, sehr zeitaufwendige Schritt der naßchemischen Bestimmungen von Holz und dessen Komponenten. Diese erfolgt mit Lösungsmitteln zunehmender Polarität wie Toluol, Benzen, Dichlormethan, Ethanol, Methanol und Wasser häufig nach Standardmethoden unter Verwendung einer Apparatur nach Soxhlet. Der Vergleich der Standardmethode mit der fortgeschritteneren Extraktionsmethode zeigte deutlich, daß der geringere Lösungsmittelbedarf und die gründlichere Entfernung des Lösungsmittels am Ende eines Extraktionsschrittes die Effektivität des nachfolgenden Waschschrittes erhöhen. Der Zeitbedarf für die Extraktgehaltbestimmung und die Standardabweichung zwischen den Wiederholungen konnten halbiert werden.

1 Introduction

Extractives-free wood is the supposition for the determination of wood components like holocellulose, cellulose, hemicellulose and lignin (TAPPI TEST METHODS; Costa e

Silva et al. 1999; Donaldson et al. 1997; Faix and Böttcher 1992; Meder et al. 1999; Rodrigues et al. 1999). Therefore the extraction of wood meal with several solvents like benzene, toluene, dichloromethane, methanol, ethanol and water is the first step during the time consuming wet chemical analysis of wood. However, also the extractives themselves and their contents are prevalently of interests.

The aim of this work was to compare the classical extraction method for the determination of the extractives contents using a Soxhlet apparatus with the advanced *flexIKA* extraction method, which is shown to speed up the extraction of wood.

2 Material and methods

2.1 Sample preparation

Wood of air dried Norway spruce (*Picea abies* (L.) Karst) was cut with secateurs, then milled with a coffee grinder (to a size of about 5 mm) and finally with a Retsch Ultra Centrifugal Mill ZM 1000 with a fixed ring sieve with a hole width of the sieve of 120 µm. Special care was taken to avoid heating of the wood during the milling process. According to TAPPI T 264 om-88 a wood sample should be extracted for 6–8 h with a mixture of benzene-ethanol (2:1 v/v) keeping the liquid boiling briskly so that siphoning from the extractor is no less than four times per hour. Samples with 3 g were extracted with benzene-ethanol (2:1 v/v), ethanol (absolute, short extraction instead of washing), ethanol (95% v/v) and finally with hot water according to TAPPI T 264 om-88 with modifications. Finally the extracted samples were air-dried for three days and subsequently oven dried to constant weight at 60 °C.

2.2 Extraction apparatus *flexIKA*

Figure 1 shows the four phases into which an extraction cycle of the *flexIKA* extraction method can be divided.

Phase 1: The weighed extraction material is fed into a prepared extraction tube. The solvent is filled into the basic vessel, a magnetic stirring rod is introduced and the extraction tube is mounted onto the basic vessel. Cooling for the bar-type cooling elements and the block-type cooling system is switched on. The experimental conditions (temperatures, number of cycles, filtration time, rev) are entered into the controller program in the PC and the process is started.

M. Schwanninger, B. Hinterstoisser (✉)
Institut für Chemie,
Universität für Bodenkultur,
Muthgasse 18, 1190 Wien, Austria
Tel.: +43-1-360066074
Fax: +43-1-360066059
e-mail: bhinter@boku.ac.at

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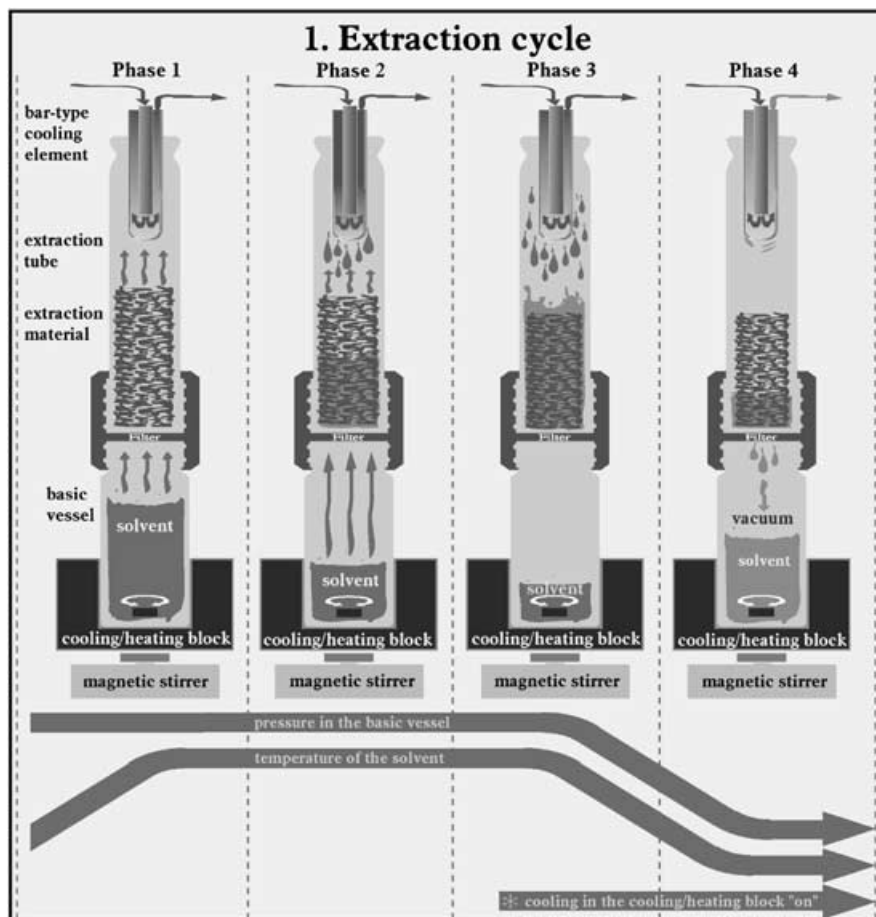


Fig. 1. An extraction cycle of the *flexIKA* extraction method can be divided into four phases. A detailed description of the functional principle is given in the material and methods section. This figure is a modification based on a picture provided by Mr. Linde from IKA-Werke GmbH & Co. KG Germany

Bild 1. Ein Extraktionszyklus der *flexIKA* Extraktionsmethode kann in vier Phasen unterteilt werden. Eine detaillierte Beschreibung des Funktionsprinzips kann unter Material und Methoden Abschnitt 2.2 nachgelesen werden. Dieses Bild wurde modifiziert und basiert auf einer Abbildung welche von Hr. Linde von IKA-Werke GmbH & Co. KG Germany zur Verfügung gestellt wurde

Phase 2: When the solvent boils the vapour penetrates the PTFE membrane filter (FF1 filter with a pore size between 10 and 20 μm were used) and the extraction material and condenses on the bar-type cooling element. This subsequent continuous stream of solvent vapour serves to heat up and vigorously fluidise the extraction material/mixed solvent at boiling temperature. This fluidised bed technic makes extraction particularly effective.

Phase 3: Heating is switched off after the set heating period has elapsed, the stirrer continues in operation and, after the solenoid valve has been opened by means of software-triggering, the cooling liquid is directed through the cooling/heating block. This results in rapid cooling of the block, the basic vessel and its content.

Phase 4: This cooling off and condensation creates a vacuum in the basic vessel and the resulting differential pressure with regard to the atmospheric pressure conveys the extractive solution through filter into the basic vessel. This cycle may be repeated any number of times. Thus the procedure may be customised for all extraction conditions.

2.3

Determination of the extractives-content

The extractives contents were determined in dependence on TAPPI T 204 om-88. Therefore the extractives were filled in weighed 250 ml flasks and evaporated to dryness on a rotovapor. Then the flasks were dried in an oven at 105 °C for 1 hour, cooled in a desiccator and

weighed to the nearest 0.1 mg. The benzene-ethanol, the ethanol 'washing solution' and the ethanol (95% v/v) extractives were determined together. The content of the hot water extractives was determined in the same way separately.

3 Results

3.1

Soxhlet and hot water extraction

To optimise the extraction with the classical method according to TAPPI T 264 om-88 a sample of spruce wood was extracted with a Soxhlet apparatus in order to proof if the recommended times are necessary. During 8 h every 30 minutes the solvent was changed and the UV-VIS spectra as well as the FT-MIR spectra of the solvent were recorded (spectra not shown). After 3 h of extraction no visible change of the spectra could be observed. Further samples were extracted with benzene-ethanol during 4 h keeping the liquid boiling briskly so that siphoning from the extractor was no less than ten times per hour. Four hours for the ethanol (95% v/v) extraction according to TAPPI T 264 om-88 were necessary. The hot water extraction on the magnetic stirrer with heating is a little bit more effective but the extraction time used for further analysis was not decreased.

3.2 Soxhlet apparatus versus *fexIKA200* extractor

3.2.1

Comparison of the spectra

An extraction with a Soxhlet apparatus was compared with a *fexIKA200* extractor in order to evaluate a possible improvement of the sample preparation process. The UV-VIS - and FT-MIR - spectra of the extractives and raffinates obtained during the extraction of spruce wood with a Soxhlet apparatus and the hot water extractives from the extraction on a magnetic stirrer and a *fexIKA200* extractor were compared in order to find suitable parameters for the extraction with a *fexIKA200* extractor. In Table 1 the results of these investigations and the parameters used for the determination of the extractives content are shown. To receive equivalent results for the benzene-ethanol extraction 5-6 cycles on the *fexIKA* were necessary, 7 cycles were used for further determinations. For the ethanol extraction 4 cycles were necessary and 5 were used. For hot water extraction two cycles were used to extract the wood meal and one additional cycle to wash it.

3.2.2

Comparison of the extractives contents

Four determinations of the extractives contents of the samples were done in parallel with a Soxhlet apparatus, a magnetic stirrer with heating and the *fexIKA200* respectively. The results compiled in Table 2A are almost identical.

3.2.3

Thermal stress

As the temperature in the *fexIKA200* is nearby the boiling point of the solvent the temperature in the Soxhlet apparatus was measured to evaluate a possible additional

thermal stress. The temperatures reached in the Soxhlet extraction tube were between 7 °C and 10 °C below the boiling point of the solvent (Table 2B).

3.2.4

Time need

The handling-time necessary for four extractions done in parallel (Table 1) and the time need for the determination of the extractives contents (Table 2C) were also ascertained, showing large differences between the two methods.

4

Discussion

Extracting with a Soxhlet 3 g of the dry sample absorbed about 30 ml of the solvent; using a *fexIKA* only 9 ml solvent was retained, meaning that more solvent is necessary for the first extraction step using a Soxhlet apparatus. As the solvent was sucked off in phase four of the *fexIKA* extraction method much less solvent was retained in the sample and the following washing step was much more effective. Hot water extraction on the plate of a magnetic stirrer with heating needs much more water than the *fexIKA* method. The time need to obtain extractives-free wood is about 14.5 hours using a Soxhlet and a magnetic stirrer compared with 10 hours using a *fexIKA*. Additionally the handling-time, as can be seen in Table 1, is incomparable higher using a Soxhlet apparatus. About 3 hours of handling-time could be saved during the extraction using a *fexIKA*. The average values of the extractives contents were almost identical with a little higher content using the *fexIKA* extractor. However, the standard deviation was about the half compared to the Soxhlet extraction.

Taking into account the longer extraction-time using a Soxhlet and on the other hand the higher temperatures

Table 1. Comparison of the extraction with a Soxhlet apparatus and a hot water extraction on a magnetic stirrer with heating with an extraction with the solids extractor *fexIKA200*. V_{in} ... Volume used for extraction; V_{out} ... Volume retained after extraction; [min. time] ... is the minimum handling-time

Tabelle 1. Vergleich der Extraktion mit Hilfe einer Apparatur nach Soxhlet und einer Heißwasserextraktion auf einem beheizbaren Magnetrührer mit einer Extraktion mit dem Feststoffextraktor *fexIKA200*. V_{in} ... für die Extraktion verwendetes Volumen; V_{out} ... Volumen welches nach der Extraktion zurückerhalten wurde; [min. time] ... minimale Zeit die für die Handhabung benötigt wird

Solvent	Soxhlet				<i>fexIKA200</i>			
	V_{in} (ml)	V_{out} (ml)	No. of cycles	Total time [min. time] (min)	V_{in} (ml)	V_{out} (ml)	No. of cycles	Total time [min. time] (min)
Benzene-Ethanol (2:1 v/v)	180	150	50-60	250 [4]	150	141	7	178 [2]
Change of solvent				30 [7]				7 [7]
Ethanol (absolute)	150	148	5	40 [4]	100	100	1	39 [2]
Change of solvent				30 [7]				7 [7]
Ethanol (95% v/v)	150	149	40-50	250 [4] 600 [26]	150	150	5	190 [2] 421 [20]
	Magnetic stirrer				<i>fexIKA200</i>			
Change of solvent				30 [7]				7 [7]
Hot water	750	700	1	60 [10]				
Filtration				60 [60]	150	150	3	180 [2]
Hot water (washing)	500	500		120 [120] 270 [197]				187 [9]

Table 2. Comparison of the classical wood extraction method with the *fexIKA* extraction method. A . . . extractives contents obtained by applying both methods; B . . . results of the temperature measurement in the Soxhlet apparatus; The temperatures were measured in the full Soxhlet extraction tubes at the end of a cycle and at the beginning when they were empty. C . . . comparison of the time need applying the standard method with the new method using a *fexIKA* solids extractor for the determination of four samples
Tabelle 2. Vergleich der klassischen Holzextraktionmethode mit der *fexIKA* Extraktionsmethode. A . . . Extraktgehalt welcher mit den beiden Methoden erhalten wurde; B . . . Ergebnis der Temperaturmessungen in der Apparatur nach Soxhlet; Die Temperaturen wurden im vollen Soxhlet am Ende eines Extraktionszykluses und nach der Entleerung am Beginn des nächsten Zykluses gemessen. C . . . Vergleich des Zeitbedarfes für die Extraktgehaltbestimmungen von jeweils vier Proben nach der Standardmethode mit der neuen Methode unter Verwendung des Feststoffextraktors *fexIKA*

A	Extractives content (%)		Extractives content (%)	
	Soxhlet	<i>fexIKA</i> 200	Magnetic stirrer	<i>FexIKA</i> 200
Solvent	organic	organic	water	water
Sample 1	2.18	2.30	1.98	1.96
Sample 2	2.28	2.34	1.95	1.94
Sample 3	2.27	2.29	1.82	2.02
Sample 4	2.35	2.27	1.83	1.93
Average value	2.27	2.30	1.89	1.96
Standard deviation	0.070	0.031	0.080	0.041

B	Benzene-Ethanol (2:1)		Ethanol (absolute)		Ethanol (95% v/v)	
	full	empty	full	empty	full	empty
Temp. Soxhlet (°C)						
Soxhlet extraction flask	77	74	85	81	87	81
Vapour phase	70	67	79	78	81	79
Soxhlet extraction tube	60	64	72	78	72	78

C	Soxhlet and Magnetic stirrer (h)	<i>FexIKA</i> 200 (h)
	Preparation of the flasks	3
Extraction with organic solvents (washing of the raffinate included)	10	7
Evaporation of the organic solvents to dryness	4	4
Hot water extraction	4.5	3
Evaporation of the water extracts to dryness	27	4
Drying of the raffinate at 105°C, cooling in a desiccator, weighing	3	3
Time need	51.5 hours	24 hours

which were reached in the *fexIKA* (Table 2B) the thermal stress for the sample should be comparable in both methods. If necessary it is possible to cool the solvent/material mixture in the *fexIKA* by sinking the cooling element into the mixture.

An additional reduction of the solvent volume should be possible using less solvent in a cycle combined with an increasing number of cycles leading to a decrease of the time need for evaporation. Half of the time could be saved using the *fexIKA* for the determination of the extractives contents (Table 2C).

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