APPLICATION OF SONOLYSIS IN THE PROCESS OF DETERMINATION OF QUATERNARY AMMONIUM SALTS IN WOOD[1]

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Content of quaternary ammonium salts in saturated pine wood was analyzed. Ammonium salts were extracted from wood using low frequency ultrasounds. Differences in the content of ammonium salts calculated from the absorption by wood and values measured analytically were observed. They resulted from strong surface active properties of cation surfactants.

Key words: quaternary ammonium salts, adsorption, pine wood, ultrasounds, sonolysis, chemical analysis.

INTRODUCTION

Effectiveness of wood protection by different conservation agents depends on their toxic effects against microorganisms, quantities of a given absorbed agent and the depth of absorption. The absorption depth can be determined using various indicators, which reveal the presence of preservatives constituents in wood. The quantity of the preservatives absorbed by wood (preservative retention) can be calculated on the basis of balance measurement of the absorbed solution. Determination of the preservative distribution in wood in different penetration, preservation zones in wood requires analytical determination of component concentrations of conservation agents in wood. The application of analytical methods for quantitative determinations of wood preservation agents involves elaboration of methods of isolation of conservation agents from

impregnated wood. The isolation of conservation agents from impregnated wood usually requires the employment of extraction methods or mineralization of examined samples. Cation surfactants, which are substances exhibiting strongly adsorptive properties on material surfaces, can easily be removed from impregnated wood by means of extraction methods. Ruddick and Sam (1984), in their studies on the concentration of didecyldimethylammonium chloride in pine wood, applied a 24 hour extraction with acetic acid in the Soxhlet apparatus. Preston et al. (1987), Zhenk and Ruddick (1995), Bürgel et al. (1996) extracted ground samples of impregnated wood with hydrochloric acid diluted in ethanol using low frequency ultrasounds. The phenomenon of low-energetic sonolysis of quaternary nitrogen bonds of ammonium salts with cellulose, hemicellulose and lignin wood constituents results in quantitative extraction of salts into the solution. The exposition of comminuted, impregnated wood immersed in liquid to ultra sounds provides the energy necessary to disrupt quaternary salt bonds with wood constituents. The process of sonolysis, depending on the fraction of the comminuted experimental material and its quantity, takes from 1.5 to 3 hours. The quaternary salt extracted from wood, depending on the expected content in the examined sample, is assayed using volumetric, spectrophotometric or chromatographic (HPLC) methods.

The objective of the performed investigations was to determine contents of quaternary ammonium and diammonium compounds (of varying structures) in pine wood employing for their extraction from wood low frequency ultrasounds.

MATERIAL AND METHODS

Assays of contents of quaternary ammonium salts in wood were carried out on pine sapwood samples (*Pinus sylvestris* L.) measuring $22 \cdot 17 \cdot 12$ mm (these samples are applied for determination of fungicidal value of wood preservatives in the screening agar-block method). The experimental material samples were saturated with solutions of four quaternary ammonium compounds of 0.25% and 0.63% concentrations using a vacuum-pressure method allowing their complete saturation. The selection of preparations took into consideration compound structural variations of cations and anions. The applied didecyldimethylammonium chloride was produced by Lonza, Switzerland:

$$C_{10}H_{21} - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - C_{10}H_{21} \quad Cl$$
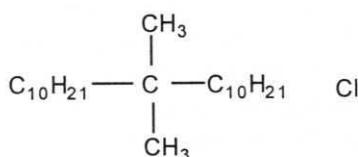
and the three of the below mentioned compounds were synthesized by prof. J. Pernak's team (Poznań University of Technology):

3-cyclohexyloxymethyl-1-decylimidazolium propionate:
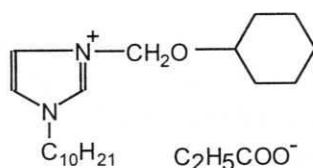
N,N'-[1,10-(2,9-dioxadecane)]bis (dimethyloctylammonium chloride):
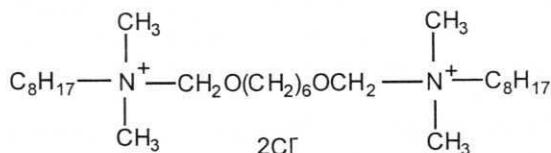
3,3'-[1,10-(2,9-dioxadecane)]-bis (1-octyloimidazolium chloride):
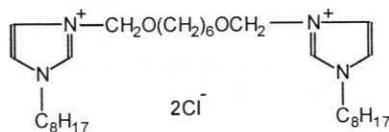
Salt retention absorbed by pine sapwood was calculated on the basis of balance measurement (absorption) of the intaken impregnation solution and also by means of two-phase titration in accordance with procedures of the following standards: AWPA 18-93, ISO 2871, PN-87/C-04818. The extraction of ammonium quaternary compounds from pine wood was performed by a three-hour exposition of comminuted experimental samples to ultrasounds (acoustic wave of 35 kHz frequency in an ultrasonic bath type Sonorex Super RK 510 H) to a fraction, which passed through a sieve with 1 mm mesh in alcohol solution of HCl. After sedimentation of the pulverized wood material for 18 hours, the clear extract was subjected to quantitative analysis with the aim to determine the content of cation active substance using the method of two-phase titration. The examined compounds were titrated with 0.002 M solution of sodium dodecylosulphate in the presence of an indicator: a mixture of dimidium bromide and disulfine blue. The standardization of the sodium dodecylosulphate was performed in accordance with AWPA 18-93 procedure using 0.002 M solution of Hyamine 1622 – (diisobutylphenoxyethoxyethyl)-dimethylbenzylammonium chloride. Simultaneously, using the same procedure and reagents, the possible content of quaternary salts in an unprotected wood was determined. In order to confirm quantitative extraction of quaternary ammonium salts from wood, samples of comminuted wood after extraction were immersed in HCl diluted in ethyl alcohol and exposed again to ultrasounds of 35 kHz frequency. Since no cation surfactants were found in the solution after repeated extraction, it was assumed that the applied 3-hour exposure to ultrasounds caused quantitative extraction of the examined surfactants from wood into the solution.

EXPERIMENTAL RESULTS

Tables 1 and 2 show contents of ammonium and diammonium salts in wood calculated from the absorption from impregnation solution and measured analytically. In the case of each pair of the examined samples, irrespective of the concentration of the impregnation solution, retention of quaternary compounds calculated from the difference of wood weights before and after saturation was smaller than the true content of the compound in wood determined analytically. Mean differences in the content of the four examined surfactants in wood, which are shown in Figures 1 and 2 and ranging from 0.32 kg/m^3 to 1.84 kg/m^3, depended on the structure of those compounds. In the case of single ammonium salts, the amount established analytically was considerably higher than the quantity calculated from the amount of the compound absorbed from the impregnation solution.

In the case of diammonium salts, these differences were considerably smaller. Strong surface acting properties of the examined quaternary ammonium and diammonium salts resulted in a selective absorption of surfactant cation solutions by wood. In the course of saturation, the concentration of ammonium salts in impregnation solutions decreased, as evidenced by data shown in Table 3.

The drop in the concentration after two saturation cycles using the vacuum-pressure method, in the case of 3-cyclohexyloxymethylo-1-decyloimidazolium propionate, ranged from 12.1% to 25%. This drop was smaller in the case of the diammo-
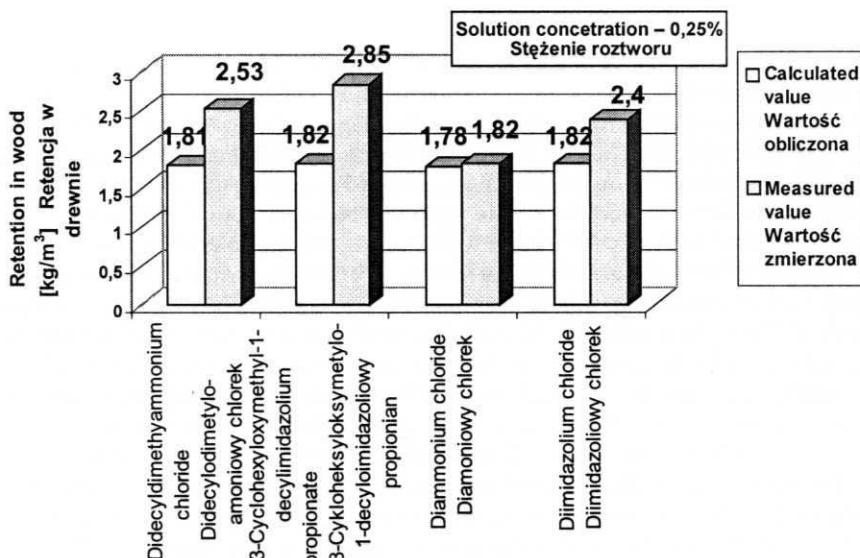
Fig. 1. Comparison of the calculated salt content absorbed
by wood with values measured analytically
Rys. 1. Porównanie obliczonej zawartości soli wchłoniętej przez drewno
z wartościami zmierzonymi analitycznie
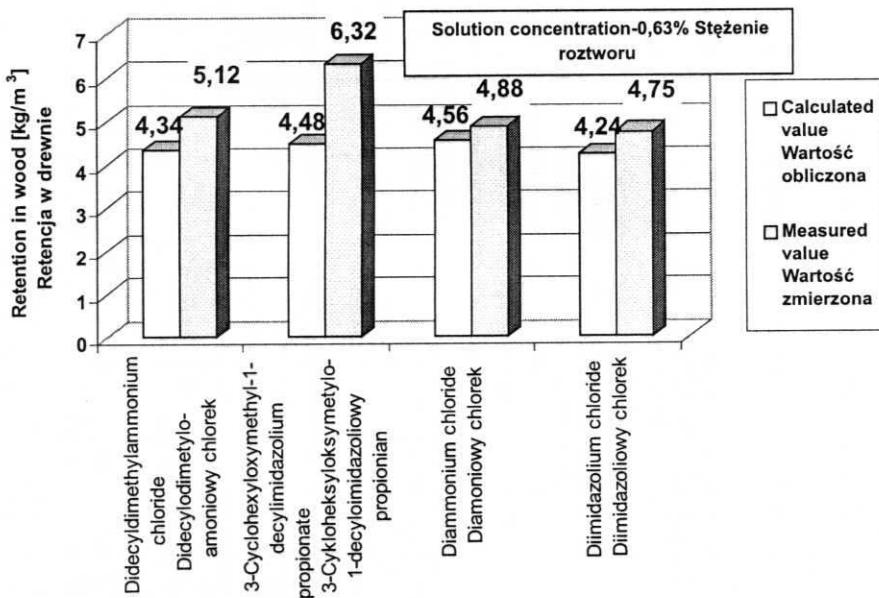
Fig. 2. Comparison of the calculated salt content absorbed by wood with values measured
analytically
Rys. 2. Porównanie obliczonej zawartości soli wchłoniętej przez drewno z wartościami
zmierzonymi analitycznie

nium salt (5.8% to 7.7%). This variation can be attributed to greater adsorption poten-
tials on wood of a single quaternary salt than of a double one. The adsorption of
3-cycloheptyloxymethylo-1-decyloimidazolium chloride at the concentration of the
impregnation solution of 12 mM/l and 6.57 pH amounted to 0.613 mM/5g of commi-
nuted pine wood (the extent of salt adsorption from solution was 50.2%). In these con-
ditions, the double salt –3,3'-[1,10-(2,9-dioxadecane)]-bis (1-octylimi-dazolium chlo-
ride) was adsorbed on wood only in 13.6% (0.163 mM/5g of comminuted pine wood).
Detailed results of investigations on the adsorption of ammonium salts on pine wood
were presented in a study prepared by Urbanik and Zabielska-Matejuk (2000).

Table 1
Tabela 1

Content of quaternary ammonium salts in wood calculated from absorption of impregnation solution and determined analytical (ultrasound extraction from wood)

Zawartość czwartorzędowych soli amoniowych w drewnie, obliczona z absorpcji roztworu impregnacyjnego oraz oznaczona analitycznie (ekstrakcja z drewna ultradźwiękami)

Compound concentration Koncentracja związku	Number of wood samples Numer próbek drewna	Number of repetitions chemical assays Ilość powtórzeń oznaczeń chemicznych	Biocide retention in wood Retencja biocydu w drewnie												
			didecyldimethylammonium chloride chlorek didecylodimetyloamoniowy						3,3'-[1,10-(2,9-dioxadecane)]-bis(1-octylimidazolium chloride) 3,3'-[1,10-(2,9-dioksadekano)]-bis (chlorek1-oktyloimidazoliowy)					
			calculated from absorption of impregnation solution obliczona z absorpcji roztworu impregnacyjnego			determined by two-phase titration (ultrasound extraction) oznaczona metodą mia-reczkowania dwufazowego (ekstrakcja ultradźwiękami)			calculated from absorption of impregnation solution obliczona z absorpcji roztworu impregnacyjnego			determined by two-phase titration (ultrasound extraction) oznaczona metodą miareczkowania dwufazowego (ekstrakcja ultradźwiękami)		
			mg (sample average) (średnio w próbce)	%	kg/m³ of wood drewna	mg (sample average) (średnio w próbce)	%	kg/m³ of wood drewna	mg (sample average) (średnio w próbce)	%	kg/m³ of wood drewna	mg (sample average) (średnio w próbce)	%	kg/m³ of wood drewna
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
0.25	1+2	I	8.203	0.344	1.827	11.036	0.463	2.458	8.244	0.322	1.837	12.554	0.490	2.797
		II				11.369	0.477	2.533				10.274	0.401	2.289
	3+4	I	8.115	0.335	1.808	11.572	0.477	2.578	8.244	0.330	1.837	10.009	0.401	2.230
		II				11.135	0.459	2.481				10.583	0.424	2.358
	5+6	I	8.059	0.338	1.796	11.370	0.477	2.534	8.011	0.320	1.785	10.625	0.424	2.358
		II				11.705	0.491	2.608				10.665	0.424	2.368
Mean x Średnia x			8.125	0.339	1.810	11.365	0.474	2.532	8.166	0.324	1.820	10.7783	0.427	2.402
Standard deviation Odchylenie standardowe ±σ			0.0724	0.0046	0.0156	0.0233	0.0115	0.0562	0.0777	0.053	0.0300	0.9038	0.0134	0.2013
Variability coefficient Współczyn. zmienności, υ %			0.89	1.35	0.86	2.23	2.24	2.23	0.95	1.63	1.65	8.39	3.17	8.38

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
0.63	7+8	I	19.606	0.790	4.352	21.940	0.884	4.889	18.689	0.770	4.164	21.091	0.869	4.699
		II				22.983	0.926	5.121				21.091	0.869	4.699
	9+10	I	19.319	0.781	4.304	23.256	0.940	5.181	18.632	9.776	4.152	21.546	0.897	4.801
		II				23.602	0.954	5.259				20.873	0.869	4.651
	11+12	I	19.555	0.795	4.356	23.594	0.940	5.257	19.729	0.764	4.396	21.895	0.847	4.879
		II				22.539	0.898	5.022				21.326	0.825	4.752
Mean x Średnia x			**19.493**	**0.789**	**4.337**	**22.986**	**0.9237**	**5.122**	**19.017**	**0.770**	**4.237**	**21.304**	**0.863**	**4.747**
Standard deviation Odchylenie standardowe ±σ			0.1530	0.0070	0.0284	0.6520	0.0271	0.1447	0.6117	0.006	0.1375	0.3700	0.0243	0.0826
Variability coefficient Współczynnik zmienności, υ %			0.78	0.90	0.66	2.83	2.94	2.83	3.25	0.78	3.25	1.74	2.82	1.74

Table 2
Tabela 2

Content of quaternary ammonium salts in wood calculated from absorption of impregnation solution and determined analytical (ultrasound extraction from wood)

Zawartość czwartorzędowych soli amoniowych w drewnie, obliczona z absorpcji roztworu impregnacyjnego oraz oznaczona analitycznie (ekstrakcja z drewna ultradźwiękami)

Com-pound concen-tration Koncen-tracja związku	Number of wood samples Numer próbek drewna	Number of repetitions chemical assays Ilość powtórzeń oznaczeń chemicznych	didecyldimethylammonium chloride chlorek didecylodimetyloamoniowy						3,3´-[1,10-(2,9-dioxadecane)]-bis(1-octylimidazolium chloride) 3,3´-[1,10-(2,9-dioksakano)]-bis (chlorek1-oktyloimidazoliowy)					
			calculated from absorption of impregnation solution obliczona z absorpcji roztworu impregnacyjnego			determined by two-phase titration (ultrasound extraction) oznaczona metodą miareczkowania dwufazowego (ekstrakcja z drewna ultradźwiękami)			calculated from absorption of impregnation solution obliczona z absorpcji roztworu impregnacyjnego			determined by two-phase titration (ultrasound extraction) oznaczona metodą miareczkowania dwufazowego (ekstrakcja z drewna ultradźwiękami)		
			mg (sample average) (średnio w próbce)	%	kg/m³ of wood drewna	mg (sample average) (średnio w próbce)	%	kg/m³ of wood drewna	mg (sample average) (średnio w próbce)	%	kg/m³ of wood drewna	mg (sample average) (średnio w próbce)	%	kg/m³ of wood drewna
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
0.25	1+2	I	8.201	0.339	1.825	13.052	0.538	2.812	7.976	0.314	1.768	6.992	0.359	1.862
		II				13.440	0.554	2.889				6.603	0.339	1.763
	3+4	I	8.117	0.337	1.817	13.154	0.542	2.834	8.004	0.328	1.800	6.977	0.358	1.858
		II				13.053	0.539	2.819				6.684	0.343	1.780
	5+6	I	8.202	0.340	1.832	13.319	0.549	2.869	7.872	0.309	1.762	7.030	0.361	1.872
		II				13.439	0.553	2.893				6.590	0.338	1.755
Mean x Średnia x			8.173	0.339	1.824	13.243	0.546	2.853	7.951	0.317	1.777	6.813	0.349	1.815
Standard deviation Odchylenie standardowe ±σ			0.0488	0.0015	0.0075	0.1808	0.0071	0.0356	0.0695	0.01	0.0204	0.208	0.0108	0.0545
Variability coefficient Współczynnik zmienności, υ %			0.78	0.90	0.66	2.83	2.94	2.83	3.25	0.78	3.25	1.74	2.82	1.74

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
0.63	7+8	I	20.355	0.816	4.488	28.543	1.185	6.360	20.689	0.870	4.356	21.091	0.914	4.855
		II				28.139	1.169	6.270				21.151	0.924	4.908
	9+10	I	19.819	0.812	4.471	28.426	1.180	6.334	20.051	0.826	4.737	21.546	0.873	4.801
		II				28.269	1.174	6.299				22.219	0.904	4.951
	11+12	I	20.258	0.818	4.482	28.080	1.166	6.257	21.232	0.792	4.588	21.896	0.887	4.879
		II				28.776	1.195	6.412				21.982	0.890	4.898
Mean x Średnia x			20.144	0.815	4.480	28.372	1.178	6.322	20.757	0.829	4.560	21.648	0.898	4.882
Standard deviation Odchylenie standardowe ±σ			0.2856	0.0031	0.0086	0.2629	0.0108	0.0574	0.5911	0.0391	0.1931	0.4619	0.01888	0.0501
Variability coefficient Współczynnik zmienności, υ %			1.42	0.37	0.19	0.93	0.92	0.91	2.85	4.71	4.23	2.13	2.09	1.03

Table 3

Tabela 3

Change in concentration of impregnation solutions of quaternary ammonium salts
after cycles of pine wood saturation

Zmiana koncentracji roztworów impregnacyjnych czwartorzędowych soli amoniowych
po cyklach nasycania drewna sosny

Compound Związek	Concentration of impregnation solution determined using two-phase titration Koncentracja roztworu impregnacyjnego oznaczona metodą miareczkowania dwufazowego			
	Initial concentration Koncentracja początkowa	Concentration after 1st saturation using vacuum-pressure method Koncentracja po I nasyceniu metodą próżnio-wo-ciśnieniową	Concentration after 2nd saturation using vacuum-pressure method Koncentracja po II nasyceniu metodą próżnio-wo-ciśnieniową	Drop in saturation after two cycles of saturation Spadek koncentracji po dwóch cyklach nasycania
	%			
3-Cyclohexyloxymethyl-1-decylimidazolium propionate	0.25	0.22	0.18	25.0
Propionian 3-cykloheksyl-oksymetylo-1-decyloimidazoliowy	0.66	0.65	0.58	12.1
Diammonium chloride	0.26	0.25	0.24	7.7
Chlorek diamoniowy	0.69	0.67	0.65	5.8

CONCLUSIONS

1. In the applied method of extraction of quaternary ammonium salts from wood using low frequency ultrasounds, a complete extraction of the biocide from wood was achieved.
2. The method of two-phase titration with the solution of sodium dodecylosulphate in the presence of dimidin bromide and disulfine blue is sufficiently sensitive for quantitative determination of more than 0.1% content of quaternary ammonium salts in wood.
3. The procedure often applied in practice of the calculation of biocide retention in wood from the absorption of the impregnation solution, in the case of surfactant cations, is burdened with an error, which depends on the adsorption capacity of these biocides in wood.
4. The content of ammonium and diammonium salts in wood measured analytically was higher than the retention calculated from the absorption of these salts by wood.

REFERENCES

AWPA – Standard A19-93 (1993): Standard for determination of quaternary ammonium compounds in wood by 2-phase titration.

Bürgel J.L., Dubois J., Ruddick J.N.R. (1996): Proposed degradation path way for quaternary ammonium compounds by mould fungi. IRG on Wood Pres. Doc. No IRG/WP 96-10166.

ISO-2871: Surface active agents-Detergents-Determination of cationic-active matter-Direct two - phase titration procedure.

PN-87/C04818 Środki powierzchniowo czynne. Oznaczanie zawartości substancji kationowo czynnej metodą miareczkowania dwufazowego.

Preston A.F., Walcheski P.J., McKaig P.A., Nicholas D.D. (1987): Recent research on alkylammonium compounds in the US. Proc. AWPA: 331-348.

Ruddick J.N.R., Sam A.R.H. (1984): Didecyldimethylammonium chloride – a quaternary ammonium wood preservative its leachability from, and distribution in, from soft woods. Mat. u. Organ. (17)4: 299-313.

Zhenk Y., Ruddick J. (1995): The effect of didecyldimethylammonium chloride on growth of different strains of mould fungus *Gliocladium roseum*. IRG on Wood Pres. Doc. No IRG/WP 95-10105.

Urbanik E., Zabielska-Matejuk J. (2000): Czynniki wpływające na adsorpcję i desorpcję czwartorzędowych soli amoniowych z drewna sosny. XIV Konferencja Naukowa WTD SGGW. Wydawnictwo SGGW: 273-278.

ZASTOSOWANIE SONOLIZY W OZNACZANIU ZAWARTOŚCI CZWARTO-RZĘDOWYCH SOLI AMONIOWYCH W DREWNIE

Streszczenie

Oznaczenie zawartości środków ochrony w drewnie wymaga opracowania sposobu ich wyodrębnienia z impregnowanego drewna. W pracy zastosowano ekstrakcję czwarto-rzędowych soli amoniowych z drewna ultradźwiękami niskiej częstotliwości (35 kHz). Analizowano zawartość czterech czwartorzędowych soli amoniowych i diamoniowych o zróżnicowanych strukturach w nasyconym drewnie sosny *Pinus sylvestris* L. Zawartość biocydów w drewnie zmierzona analitycznie metodą miareczkowania dwufazowego jest większa od ilości obliczonej z wchłonięcia tych soli przez drewno. Wynika to ze zdolności do adsorpcji kationowych surfaktantów na drewnie.

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