

SYSTEMATICAL ERRORS BY DETERMINING WOOD PRESERVATIVES

SYSTEMATISCHE FEHLER BEI DER BESTIMMUNG VON HOLZSCHUTZMITTELN

ERREUR SYSTEMATIQUES LORS DE LA DETERMINATION DE PRODUITS PRESERVATEURS DE BOIS

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Summary

The present paper shows results of measurements of Pentachlorophenol and γ -Hexachlorocyclohexane in wood, dust and indoor air. All samples were taken from a highly contaminated building (constructed 1970). For wood as well as for indoor air it can be shown, that the obtainable average concentrations are in the order of magnitude of the resulting standard deviations. Contaminated wooden boards, taken from a coherent part of the ceiling were used as samples for an inter-laboratory test. Single results for PCP in this test vary from 10 up to 1500 mg/kg. In average a PCP concentration of 495 mg/kg is detectable. The calculated standard deviation is 385 mg/kg. In the same building indoor air samples were collected. "Amberlite XAD" and "Florisil" were used as absorbents. All samples were collected within a 48 hour period. Within this period PCP- and γ -HCH- concentrations in indoor air vary widely. For PCP indoor air average concentrations between 2.9 and 6.9 $\mu\text{g}/\text{m}^3$ are detectable. The γ -HCH concentrations vary from 1.9 to 10.7 $\mu\text{g}/\text{m}^3$. Increasing humidity leads to higher γ -HCH concentrations in indoor air. In total all presented results prove the considerable problems judging possible health risks resulting from wood preservatives like PCP and γ -HCH.

Zusammenfassung

Die vorliegende Arbeit zeigt Ergebnisse der Messungen der Holzschutzmittel Pentachlorphenol (PCP) und γ -Hexachlorcyclohexan (γ -HCH; Lindan) in Holz, Staub und Innenraumluft. Alle Proben stammen aus einem deutlich holzschutzmittelbelasteten Bauwerk (Baujahr 1970) und wurden unter praxisnahen Bedingungen genommen. Sowohl bei Holz als auch bei Innenraumluft liegen die erzielbaren Mittelwerte in

der Größenordnung der jeweiligen Standardabweichungen. Aus dem Material einer Holzdecke wurde ein zusammenhängendes Stück entnommen (Gesamtfläche ca. 2.5 m²) und daraus Proben für einen Ringversuch zur Bestimmung von PCP in Holz gewonnen. Dabei zeigte sich deutlich, daß zusätzlich zu Differenzen aus der analytischen Bestimmung von PCP in diesen Proben ein erheblicher Unterschied in den Einzelgehalten der Proben gefunden werden kann. Der Mittelwert für alle Proben beträgt 495 mg PCP/kg Holz bei einer Standardabweichung von 77 %. Die Einzelwerte schwanken von 10 bis 1500 mg/kg. Im gleichen Gebäude wurden PCP und γ -HCH in der Innenraumluft gemessen. Über einen Meßzeitraum von 48 h verändern sich die meßbaren Gehalte an PCP und γ -HCH in der Innenraumluft deutlich. Je nach Meßort konnten PCP-Mittelwerte von 2.9 bis 6.9 $\mu\text{g}/\text{m}^3$ gefunden werden. Die Standardabweichungen lagen zwischen 25 und 40 %. Bei γ -HCH konnte gezeigt werden, daß Raumtemperatur und relative Luftfeuchte einen sehr deutlichen Einfluß auf die Konzentration dieses Biozides in der Innenraumluft haben. Unter Normalbedingungen (ca. 20°C und 40 bis 50 % rel. Feuchte) wurden γ -HCH-Gehalte von ca. 1.5 $\mu\text{g}/\text{m}^3$ gemessen. Die Standardabweichung dieser Messungen beträgt ca. 40 bis 80 %. Bei hohen Luftfeuchten (80 % rel.) steigt der Gehalt an γ -HCH auf 8 bis 10 $\mu\text{g}/\text{m}^3$ an. Insgesamt belegen die vorgelegten Ergebnisse die erheblichen Unsicherheiten bei einer möglichen Bewertung potentieller Gesundheitsrisiken durch Holzschutzmittel in Innenräumen.

Résumé :

Le travail présent montre les résultats de mesure déterminé avec pentachlorophenol et γ -cyclohexane d'hexachlorure dans le bois, la poussière et l'air intérieur. Toutes les éprouvettes ont été prélevées d'un bâtiment contaminé (construit en 1970). La comparaison des résultats déterminées pour le bois ainsi que l'air intérieur a montré que les concentrations moyennes atteignent l'ordre de grandeur des différences standard. Des planches contaminées prises d'une partie cohérente du plafond ont été utilisées pour un essai inter-laboratoire. Les résultats déterminés dans cet essai avec le PCP variaient de 10 à 1500 mg/kg. On a déterminée une concentration moyenne en PCP de 495 mg/kg. La différence

standard calculée est de 385 mg/kg. Des éprouvettes d'air étaient prélevées du même bâtiment. "Amberlite XAD" et "Florisorb" ont été utilisés en tant qu'absorbant. Toutes les éprouvettes ont été prélevées dans une période de 48 heures. Pendant cette période les concentrations en PCP et γ -HCH dans l'air intérieur variaient extrêmement. Pour le PCP dans l'air les concentrations variaient entre 2,9 et 6,9 $\mu\text{g}/\text{m}^3$. Une humidité plus élevée mène à des concentrations plus élevées en γ -HCH de l'air intérieur. En total tous les résultats présentés démontrent les problèmes considérables qui existent à juger les risques éventuelles pour la santé provenant de produits préservateurs du bois comme PCP et γ -HCH.

Key Words

Wood preservatives , Pentachlorophenol, γ -Hexachlorocyclohexane, Wood, Dust, Indoor Air

Introduction

The determination of wood preservatives like PCP or γ -HCH in wooden boards, dust or indoor air is normally accompanied by a lot of problems. The comparison of analytical results of different laboratories for wood preservatives in contaminated boards, indoor dust or indoor air can lead to widely differing results. Due to experiences with formaldehyde or asbestos a lot of people regarded the distribution of wood preservatives in wood as homogeneous. It was not considered, that wood preservatives often had been parts of coats of colour or varnish. In most cases the origin of contaminated boards is unknown as well as their absorptive capacity for colours or varnish. In the past solid samples taken from contaminated wooden boards had not been defined. The measured concentration depends on the thickness of the taken sample(1,2). Results without any information about the sample geometry are not comparable. Comparable problems are given by determining biocides in indoor dust. It can be proved, that there is a difference between the concentration of wood preservatives in dust collected with a vacuum cleaner or of deposited dust collected with a brush. Biocides in indoor air are normally collected on different absorbents like silica gel or various types of polymers like

polyurethan foam(3) or "Amberlite XAD-2"(4). For the evaluation of indoor air quality normally few (less than 4) samples were collected. Very often other important parameters for indoor air quality like room temperature, humidity, parameters resulting from the buildings like age, types of windows, doors etc. as well as the outside weather conditions were not regarded. All these factors characterize dynamic processes in indoor air and determine the indoor air quality(5,6). For formaldehyde for example it can be shown, that at least 10 measurements are necessary to determine the concentration of formaldehyde in indoor air correctly (5).

Determination of wood preservatives like Pentachlorophenol (PCP) and γ -Hexachlorocyclohexane (γ -HCH) in wooden boards and in dust

Table 1 shows the relation of the thickness of a sample and the concentration for wood preservatives like PCP and γ -HCH in wooden boards taken from a contaminated building. Like in other studies mentioned (1,2) the results proof, that about 90 % of the total biocide amount is concentrated in the surface layers (0-2 mm) of wooden boards. If the sample thickness varies from about 100 % (thickness 0-1 mm compared to thickness 0-2 mm) the biocide concentration varies from 30 % for PCP to about 80 % for γ -HCH.

Table 1

Concentrations of Pentachlorophenol and γ -Hexachlorocyclohexane in wood in proportion to the thickness of wood samples taken from boards treated with wood preservatives

Thickness of wooden sample in mm 0 = board surface	Concentration of PCP in mg/kg n=5	Concentration of γ -HCH in mg/kg n=5
0 - 1	385 \pm 18	48 \pm 12
0 - 2	282 \pm 15	9 \pm 3
0 - 4	150 \pm 23	6 \pm 4
2 - 4	21 \pm 9	2 \pm 1

In addition to this effect it can be determined, that even if the thickness of the samples are fixed to 2 mm (0 = board surface) the concentration of wood preservatives in contaminated wood can vary widely. Table 2 shows the results for PCP measured in boards taken from a wooden ceiling. All samples had been taken from coherent boards of a pretreated wooden ceiling. The boards were treated with a wood preservatives in the year 1970. The concentration range for PCP in these wooden boards varies from 170 to 730 mg/kg (sample area about 50 cm²; thickness 2 mm).

Table 2

Measured Pentachlorophenol(PCP) concentrations in boards treated with wood preservative taken from a contaminated building. The thickness of the examined wooden layer was 2 mm for each sample and the area of the samples was about 50 cm². Results of our own laboratory compared to results from several other laboratories (single results from an inter-laboratory test (7)).

Sample (Number)	Results from the FMPA laboratory PCP in mg/kg	Results from other laboratories for the same board PCP in mg/kg
2	657	191
7	406	33
8	616	355
13	649	880
17	567	315
25	285	237
31	242	545
32	657	325
33	170	267

To demonstrate the unsatisfactory situation by determining wood

preservatives in wooden boards, samples from this contaminated ceiling were analysed by other laboratories. In total 14 laboratories took part in an inter laboratory comparison(7). The total sample area was approximately 2.5 m². Each laboratory got two boards for the determination of PCP. Some single results for different boards are already shown in table 2. The analysed concentrations for PCP in these samples varied from 10 to 1500 mg/kg. Table 3 gives a view to the average concentration and the standard deviation for PCP in wooden boards and dust in a contaminated building.

Table 3
Average Pentachlorophenol(PCP)concentrations in boards treated with PCP as wood preservative and passively collected dust taken from a contaminated building. Results of an inter laboratory test.

Samples	Average concentration of PCP in mg/kg	Standard deviation in mg/kg
Boards		
Result from our own laboratory	457	173 (n = 17)
Results from other laboratories	495	385 (n = 24)
Dust (deposited, collected by brush)		
Results from our own laboratory	249	18 (n=3)
Results from other laboratories	316	102 (n= 16)

PCP in wood preservatives is normally accompanied by other biozides. In the boards of the ceiling approximately 25 mg/kg γ -HCH, about 15 mg/kg Dichlofluamid and 12 mg/kg poly-chlorinated-dioxins and -dibenzofurans (PCDD and PCDF) can be found in addition to PCP (8). Normally deposited dust is an excellent indicator for the use of biozides in a building. In this

special case following biocides are found in the deposited, old dust: PCP 300 mg/kg; γ -HCH 5 mg/kg; PCDD/PCDF 12 mg/kg ; Dichlofluanid 23 mg/kg; PCB 190 mg/kg. Collected with a vacuum cleaner the concentration of PCP in this dust decreases to 10 to 40 mg/kg. Parallel to the determination of PCP in wood the concentration of PCP in dust was also determined by other laboratories. The dust (total amount about 75 g) was collected by a brush from the surface of spars inside the building, the boards were taken from. This dust was expected to be more homogenous than the boards and the results can give an idea to the analytical quality of the participating laboratories. Our own results as well as the results of the other laboratories verify that the deposited dust can be used as standard for the analytical quality for the determination of PCP (see table 3).

Determination of pentachlorophenol and γ -hexachlorocyclohexane in indoor air.

In addition to the determination of wood preservatives in wood and dust, samples of indoor air were taken in the concerned rooms and the concentrations of wood preservatives (PCP and γ -HCH) were determined. Samples of indoor air were taken in rooms of various volumes under normal conditions as well as under increased temperature or/and humidity. Various adsorbents were tested under these conditions. The building was closed for six weeks before the sampling was carried out and kept closed during the campaign. In two rooms (a hall: volume > 500 m³; an office room: volume < 50 m³) of this building the indoor air concentrations of wood preservatives were determined. Under normal conditions (temperature about 20 °C, humidity about 40 to 50 % rel.) it can be shown, that no significant difference between silicagel and Amberlite XAD if used as adsorbents for PCP and γ -HCH can be determined. All possible effects are overlaid by dynamic processes in indoor air. Over a 48 hour period the average concentration for PCP in the air of the hall was 6.9 $\mu\text{g}/\text{m}^3$ with a standard deviation of $\pm 2.7 \mu\text{g}/\text{m}^3$. The concentration for γ -HCH in the air varies from 0.4 to 2.6 $\mu\text{g}/\text{m}^3$ (average concentration 1.4 $\mu\text{g}/\text{m}^3$). In the air of the office the average concentrations for PCP was lower (average concentration 2.9 $\pm 0.7 \mu\text{g}/\text{m}^3$) and comparable for γ -HCH (average concentration 1.9 $\pm 0.3 \mu\text{g}/\text{m}^3$) (8). If temperature or humidity of indoor air are increased the concentrations of PCP and γ -HCH rise equally. Table 4 gives a view to the effects of humidity and room temperature for the indoor air quality. The results for γ -HCH demonstrate, that increased

humidity and room temperature lead to concentrations of γ -HCH in indoor air, which are significant higher than at normal indoor air conditions.

Table 4

Concentrations of PCP and γ -HCH in indoor air at higher room temperatures and humidities. Absorbent Amberlite XAD 2 and silicagel/charcoal

Room temp. °C	Humidity % rel.	Average PCP in $\mu\text{g}/\text{m}^3$	Average γ -HCH in $\mu\text{g}/\text{m}^3$
Absorbent Amberlite XAD-2			
26	80	2.8	8.0
32	60	2.1	10.7
35	30	3.2	2.7
Absorbent Silicagel/Charcoal			
26	80	1.4	1.7
32	60	1.4	3.2
35	30	2.4	1.5

Discussion

The presented results proof, that the average indoor air concentration of PCP and γ -HCH is varying in the order of magnitude of the standard deviation for the total proceeding . In a later investigation the standard deviation of the method was determined. It can be demonstrated that the standard deviation for the determination of PCP and γ -HCH is approximately 10% using PU-foam or Amberlite XAD as absorbents for air sampling. The sampling time for these investigations was about 4 hours (5). The presented data show clearly, that the local indoor-air-concentration during the sampling time (48 h) have a great variation. These deviations overlay at standard conditions the differences in the collection efficiency of the different adsorbents. At higher temperatures and overall at higher humidities these differences become more evident, especially using silicagel in combination with charcoal. Activated charcoal placed after silicagel, is always contaminated with various amounts of PCP(9). This

fact demonstrates that silicagel should not be used for sampling PCP and γ -HCH in indoor air. The large standard deviations determining wood preservatives in wood, dust and indoor air proof, that there will be a lot of problems to give a view to the possible risks of indoor air pollution. Neither the simple determination of wood preservatives in solid material nor the determination of biocides in indoor air can be used for a simple scale to judge risks of health resulting from semivolatile biocides. The concentration range for PCP in boards taken from one part of a ceiling in a contaminated building demonstrates that all data for biocide concentration in wood have to be looked on very critical. The differences by painting and the differences of the absorptive capacity of wood lead normally to results presented in this work. The indoor air quality depends mainly on dynamic effects of indoor air. Measurements lasting longer than four to six hours point out, that data resulting from a few short-period measurements can lead to wrong results.

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