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ORIGINAL

Suitability of analytical methods to determine tebuconazole, propiconazole and permethrin in aged wood samples

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Abstract
The suitability of common analytical methods for the determination of active substances from wood preservatives in aged wood samples was investigated during an interlaboratory study. Permethrin, propiconazole and tebuconazole were quantified in 1.5 and 8 year-old wood samples by gas chromatography and liquid chromatography. Generally, the applied methods yielded reliable results for these samples. However, wood components can coelute with propiconazole and tebuconazole during liquid chromatography. Optimization of separation might be required if UV detection is applied.

1 Introduction

Chromatographic methods are commonly applied to determine the contents of organic wood preservative components (active substances) in treated wood. The analytical procedures are usually developed and validated using fresh samples of wood that have been doped with a defined amount of the target compounds.

However, this practice cannot indicate changes in recovery rates and precision of the methods that could potentially be caused by chemical changes in the wood during its service life. Indeed, analytical laboratories very often get samples of wood that has been in service in order to investigate, for example, the correct treatment of wood regarding the achieved penetration and retention.

Three active substances, i.e., permethrin, propiconazole and tebuconazole (see Fig. 1 for chemical structures), were selected to study the suitability of commonly applied analytical methods for the analysis of aged wood. These active substances were approved for marketing in wood preservatives according to the European regulations [Biocidal Products Directive (BPD, Directive 98/8/EC 1998), replaced by Biocidal Products Regulation (BPR, Regulation (EU) No. 528 2012). Permethrin acts as an insecticide, and propiconazole and tebuconazole are widespread fungicides in currently produced wood preservatives. The assessment reports for permethrin (European Chemicals Agency 2014), for propiconazole (European Chemicals Agency 2007a) and for tebuconazole (European Chemicals Agency 2007b) list

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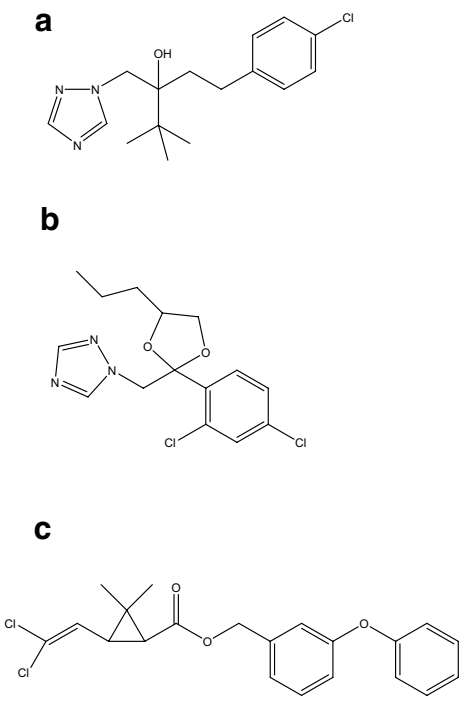

Fig. 1 Structures of **a** tebuconazole, **b** propiconazole and **c** permethrin

gas chromatography using flame ionization detector (GC-FID) as suitable technique to analyze these active substances in traded formulations. Gas chromatography coupled to mass spectrometry (GC–MS), electron capture detector (GC-ECD), nitrogen/phosphorus detector (GC-NPD) and high performance liquid chromatography coupled to UV detector (HPLC–UV) or mass detectors (HPLC–MS/MS) are listed as methods to analyze residues of at least one of these active substances in soil, air and water. A standardized liquid chromatography tandem mass spectrometry (LC–MS/MS) method (EN 15637 2008) is available for the analysis of pesticide residues in foods of plant origin.

Interlaboratory studies between European laboratories using GC- and HPLC-methods to analyze propiconazole in treated wood were initiated by CEN/TC 38 'Durability of wood and wood-based products'. The methods proved to be suitable and were reported as CEN/TR 16420 (2012). Standard methods for the determination of propiconazole, tebuconazole and permethrin are provided by the American Wood-Preservers' Association (A28-14, A42-14, A48-15; AWPA 2018a, b, c). Results of an interlaboratory study of several German and Austrian laboratories on the determination of permethrin in wood were published by Schoknecht et al. (2008). The applied methods are provided on the website of the 'RAL-Gütegemeinschaft: Imprägnierte Holzbauelemente e.V.' (2012a, b, 2013a, b).

HPLC methods can also be applied to analyze active substances in wood preservative formulations as described by Hill (2012). Mauruschat et al. (2014) applied gas chromatography coupled to field asymmetric ion mobility spectrometry (GC-FAIMS) for fast detection of organic active substances in recovered wood. Miyauchi et al. (2005) applied solid-phase extraction to remove wood extractives from different conifer species that co-eluted with cyproconazole and tebuconazole. A detailed description of the method development for a GC–MS method to analyze tebuconazole, propiconazole, 3-iodo-propynyl butylcarbamate and permethrin in commercially treated wood was published by Šťávová et al. (2011).

However, there is a lack of knowledge of the suitability of these methods to precisely quantify these substances in aged wood. First experiences from an interlaboratory comparison between ten laboratories are reported in this article. Analytical methods that are regularly applied in these laboratories were used to quantify the selected active substances in treated wood. Subsamples of three differently aged wood samples were distributed and analyzed in parallel by HPLC–UV, HPLC–MS, GC-FID, GC-ECD and/or GC–MS. Particular attention was paid to possible matrix effects.

2 Materials and methods

2.1 Wood samples

Samples A and B belong to the same batch of treated pine sapwood [samples of $50 \times 5 \times 2.5$ cm^3 treated by vacuum impregnation with a waterborne wood preservative (water-dilutable concentrate)]. Original amounts of tebuconazole and propiconazole were calculated from the retention of the wood preservative and concentrations of the active substances in the preservative formulation to be 160 mg kg^{-1} (each).

Sample A was stored for 8 years at room temperature in a dark room (cellar), whereas sample B was exposed to soil contact under natural weathering conditions for 6 years, and then stored under the same conditions for another two years in the same way as sample A.

Sample C originated from a board of pine sapwood that was vacuum-impregnated with a water-borne wood preservative (water-dilutable concentrate) containing propiconazole, tebuconazole and permethrin. Original concentrations were calculated to be 80 mg kg^{-1} both for propiconazole and tebuconazole and 140 mg kg^{-1} for permethrin. Sample C was stored at room temperature in the dark for 1.5 years. All samples were pre-crushed by a shredder and then milled by a cutting mill (SM 2000, Retsch) without cooling to grain size < 1 mm (sample A and B) and blades with two

dimensions < 1 mm (sample C) before distribution to the participants.

A sample of freshly milled, 1–2 year-old untreated pine sapwood was provided by one participant (matrix A). A second sample of untreated wood originated from an interlaboratory study that was performed in 2004 (matrix B). Subsamples of matrix B have been stored in several laboratories in the dark at room temperature and were distributed to all participants.

For comparison, analysis was also performed on spruce samples that were analyzed during former interlaboratory studies and have been stored at room temperature in the dark for up to 13 years.

2.2 Sample preparation

The milled wood samples were extracted by each participant. In general, 20 ml of methanol was added to 1 g of wood and sonicated for 2 h at a temperature not exceeding 50 °C. 10 ml methanol was added to 1 g of wood in two laboratories. The extracts were filtered through PTFE and directly injected. Methanol was used for dilution if necessary. Extraction conditions applied in the different laboratories are presented in Table S2 (in Electronic Supplementary Material).

2.3 Analytical methods

Different types of reversed-phase columns from different suppliers were used to separate substances by HPLC and UHPLC (ultra high performance liquid chromatography). Gradient elution was performed by different mixtures of eluents at room temperature, 35 or 40 °C, respectively. The duration of the methods varied between 5 and 40 min. Usually, diode array detectors were applied to determine the analytes. Detection wavelengths for propiconazole and tebuconazole were either 210, 223 or 225 nm. Permethrin was detected at 210, 215, 223 or 225 nm. In one laboratory, quantification was performed by a single quadrupole mass spectrometer (LC–MS). The following signals were used for quantification: *m/z* 342 for propiconazole, *m/z* 308 for tebuconazole, and *m/z* 245 for permethrin.

Gas chromatography was performed on hydrophobic stationary phases in different columns. Samples were diluted in methanol (toluene in one laboratory) if necessary and injected either in split or splitless mode. The duration of the methods ranged between 11 and 28 min.

Electron capture detection was applied to quantify propiconazole and permethrin (in one laboratory also tebuconazole), whereas tebuconazole was quantified by flame ionization detection in other laboratories. All three analytes were quantified by mass spectrometry (electron ionization). Detected masses were *m/z* 259 for propiconazole (*m/z* 261, 173 or 179 as qualifiers), *m/z* 250 for tebuconazole (*m/z* 125, 252 or 163 as qualifiers) and *m/z* 183 for permethrin (*m/z* 163 and 165 as qualifiers). The applied columns and temperature programs are presented in Table S4. Mass spectra are presented in Figure S1 (in Electronic Supplementary Material).

External calibration was applied to HPLC as well as GC methods. Analytical standards for tebuconazole (CAS: 107534-96-3), propiconazole (CAS: 60207-90-1), and permethrin (CAS: 52645-53-1) were obtained, for example from Sigma-Aldrich and Dr. Ehrenstorfer. The standard substances were dissolved in methanol at concentrations between 0.05 and 25 mg l^{-1} depending on the sensitivity of the analytical method. For some experiments, the standard substances were also dissolved in methanolic extracts of the untreated samples from matrix A and matrix B (hereafter referred to as 'matrix calibration'). All analytical results are related to air-dried wood samples. Further details on LC and GC methods applied in the different laboratories are presented in Tables S3 and S4 (in Electronic Supplementary Material).

2.4 Series of experiments

Two series of experiments were performed. During the first series, propiconazole, tebuconazole and permethrin were quantified in the three aged wood samples by HPLC and GC methods that are commonly applied in the participating laboratories.

Altogether, six laboratories applied HPLC–UV, one laboratory applied UHPLC-UV, and one laboratory performed LC–MS analysis. Two laboratories applied GC–MS, four laboratories applied GC-ECD for propiconazole and permethrin, one laboratory applied GC-ECD to tebuconazole, and two laboratories applied GC-FID to tebuconazole. Analysis of sample C was repeated due to contradictory effects of matrix calibration on the results for tebuconazole and propiconazole from HPLC methods. Results from eight laboratories were compared for calibration based on analytical standards in methanol and matrix calibration using the two samples of untreated wood (freshly milled matrix A and matrix B from 2004).

3 Results and discussion

3.1 Residual contents of propiconazole, tebuconazole and permethrin in aged wood samples

The analyzed contents of propiconazole and tebuconazole were lower than the amounts calculated on the basis of the preservative uptake for the two samples that were treated 8 years prior to the analysis. The analyzed concentrations

are summarized in Table 1 (HPLC) and Table 2 (GC). The results from the different methods ranged between 117 and 142 mg kg^{-1} for propiconazole and between 114 and 142 mg kg^{-1} for tebuconazole for sample A, representing 73–89% and 71–89% of the original amounts of propiconazole and tebuconazole, respectively (see Table S5 in Electronic Supplementary Material). The range of the results was slightly lower for sample B, i.e., 100–140 mg kg^{-1} propiconazole and 85–120 mg kg^{-1} tebuconazole, representing 62–88% and 53–75% of the original amounts of propiconazole and tebuconazole, respectively (see Table S6).

During the first series of experiments, the results from the different methods ranged between 69 and 86 mg kg^{-1} for propiconazole, between 58 and 69 mg kg^{-1} for tebuconazole and between 146 and 167 mg kg^{-1} for permethrin for sample C, representing 86–108%, 73–93% and 104–119% of the original amounts of propiconazole, tebuconazole and permethrin, respectively (see Table S7).

Table 1 Content of the target substances in wood—results from HPLC analysis

Sample	Analytical procedure	Solvent for calibration solutions	Propiconazole			Tebuconazole			Permethrin		
			n	Mean	SD	*n*	Mean	SD	*n*	Mean	SD
				mg kg^{-1}	mg kg^{-1} *(%)*		mg kg^{-1}	mg kg^{-1} *(%)*		mg kg^{-1}	mg kg^{-1} *(%)*
A	HPLC–UV (Series 1)	Not specified	8	125	28 *(22)*	8	114	29 *(25)*			
B		Not specified	8	128	32 *(25)*	8	108	27 *(25)*			
C		Not specified	8	75	24 *(32)*	8	67	26 *(39)*	7	147	12 *(8)*
C	HPLC–UV (Series 2)	Methanol	9	65	8 *(12)*	6	58	7 *(13)*	8	130	14 *(11)*
		Pine extract A	5	66	8 *(12)*	2	59		5	131	4 *(3)*
		Pine extract B	8	71	11 *(16)*	6	58	9 *(15)*	8	130	5 *(4)*
A	LC–MS (Series 1)	Methanol	1	141		1	120				
B		Methanol	1	140		1	117*				
C		Methanol	1	86		1	69				

Calculated original amounts in samples A and B were 160 mg kg^{-1} both for propiconazole and tebuconazole. Calculated original amounts in sample C were 80 mg kg^{-1} both for propiconazole and tebuconazole and 140 mg kg^{-1} permethrin

n is the number of method variations applied

**t* test including all measured values indicated that analyte content in sample B is lower than analyte content in sample A ($\alpha = 0.05$, one-sided test of null hypothesis A = B, homogeneity of variance assumed)

Table 2 Content of the target substances in wood—results from GC analysis

Sample	Analytical procedure	Propiconazole			Tebuconazole		Permethrin		
		n	Mean	SD	*n*	Mean	*n*	Mean	SD
			mg kg^{-1}	mg kg^{-1} *(%)*		mg kg^{-1}		mg kg^{-1}	mg kg^{-1} *(%)*
A	GC-ECD	3	124	3 *(2)*	1	132			
B		3	109*	13 *(12)*	1	108			
C		3	69	5 *(7)*	1	58	3	161	14 *(9)*
A	GC–MS	2	142		2	142			
B		2	133*		2	119*			
C		2	78		2	74			
A	GC-FID				1	115			
B					1	85*			
C					1	64			

Calculated original amounts in samples A and B were 160 mg kg^{-1} both for propiconazole and tebuconazole. Calculated original amounts in sample C were 80 mg kg^{-1} both for propiconazole and tebuconazole and 140 mg kg^{-1} permethrin

n is the number of method variations applied

**t* test including all measured values indicated that analyte content in sample B is lower than analyte content in sample A ($\alpha = 0.05$, one-sided test of null hypothesis A = B, homogeneity of variance assumed)

The applied analytical methods were selected according to available equipment and methods in the different laboratories. During this study, it was not intended to prioritize a certain procedure but to identify specific aspects of the different methods when applied to the same analytical task. In addition, results of different analytical methods can hardly be compared since the correct values of analyte concentrations in the aged wood samples are not known.

It can be expected that analytes and matrix components from wood extracts can be easier separated by GC methods due to higher separation potential compared to LC methods. Specific detection by mass spectrometers compared to less specific detectors like ECD, FID and UV allows separation of analyte signals from matrix components, both for GC and LC methods. Further aspects like the solvent in which the sample is diluted might affect the selection of analytical methods.

Statistical evaluation of the reported data (two-sample *t* tests, 95% confidence level, two-sided test, homogeneity of variance assumed) did not indicate differences between the results of the different analytical methods for the three analytes in the investigated wood samples. It should be noted that standard deviations between results from different laboratories for HPLC-analysis of permethrin and for GC-analysis of all three analytes were below 10% with only two exceptions, whereas standard deviations of HPLC–UV results were in the range of 20–40% for the analysis of propiconazole and tebuconazole, which points to analytical difficulties that are specially related to the analysis of tebuconazole and propiconazole from wood extracts by HPLC–UV. Intralaboratory standard deviations were available only from a few laboratories. Values were usually below 5% for all applied analytical methods, indicating that the analytical procedures themselves were robust.

3.2 Recovery rates of applied methods

In one laboratory, wood samples were analyzed directly after addition of 150 mg kg^{-1} of propiconazole, tebuconazole and permethrin for preliminary tests. Recovery rates were between 91 and 101% for the applied GC–MS-, GC-ECD-, GC-FID-, LC–MS- and HPLC–UV-methods.

The recovery rates were improved by 1–3% by repeated extraction of the wood samples. It was concluded that one single extraction step is appropriate for the extraction of these analytes since repeated extraction can be a source of increased measurement uncertainty. According to the results from one laboratory, lower extraction yields were observed if the wood samples were extracted with toluene (data are not presented).

Higher volumes of solvent per mass of wood can possibly improve yields during extraction. However, results for the two different ratios between solvent volume and wood mass were in the same range. No systematic effect on the test results was observed if either 10 or 20 methanol was added to 1 g wood sample for extraction (see Tables S2 and S5 to S9 in Electronic Supplementary Material).

Recovery rates between 96 and 103% were observed in interlaboratory tests on milled wood samples that were doped with tebuconazole, propiconazole and permethrin. The applied analytical methods were similar to the methods applied in this study, i.e., extraction in methanol by a single sonication step and direct analysis of filtered extracts by GC and HPLC (see Table 3).

Šťávová et al. (2011) compared different extraction methods for tebuconazole, propiconazole, iodo-propynyl butylcarbamate and permethrin from wood. All procedures included several sample preparation steps and solid phase extraction followed by GC–MS analysis. Recovery rates of the most efficient procedures were 86% for tebuconazole, 85% for propiconazole and 78% for permethrin if methanol was used for extraction. The recovery rates could be improved by the use of acetone and were about 100% if acetone extraction was combined with a Soxhlet procedure. Kukowski et al. (2017) applied stepwise extraction of wood samples to first extract 'loosely bound' tebuconazole (about 85%) by sonication and then 'strongly bound' tebuconazole by subsequent Soxhlet extraction (about 15%) using acetone as extraction solvent.

3.3 Matrix calibration for HPLC-methods

In general, matrix calibration can be helpful to avoid incorrect calculation of concentrations in chromatograms due to interfering signals. For instance, target substances can adsorb to binding sites in the injector, and labile compounds can decompose during injection for gas chromatography. These effects can be avoided due to matrix-induced response enhancement (Poole 2007). Equal conditions for samples and calibration standards can be ensured by matrix calibration. Matrix calibration is also a way to ensure equal ionization conditions both for standards and samples in LC–MS methods (Zrostlikova et al. 2002).

Two laboratories applied calibration using standard substances solved in methanol compared to standard substances solved in methanolic extracts of untreated pine wood samples (matrix calibration). Contrary effects were observed for the two untreated wood samples of different origin. In one laboratory, the calculated result was higher for matrix calibration, while it was reverse in the other one. It was assumed that this was caused by differences between the wood samples that were used to prepare the matrix extracts. Therefore, analysis was repeated by means of one of the aged wood samples in all laboratories using two defined untreated wood samples (matrix A and B) to clarify whether matrix calibration can be recommended for HPLC–UV-analysis of

Table 3 Comparison of results for wood samples of different age

Experiment	Sample	Method	Calculated original content			Analyzed content		
			Propiconazole	Tebuconazole	Permethrin	Propiconazole	Tebuconazole	Permethrin
			mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
Series 1	A	GC and HPLC	160	160		124–142	114–142	
	B	GC and HPLC	160	160		109–133	85–119	
	C	GC and HPLC	80	80	140	69–86	58–74	147–167
Series 2	C	HPLC–UV				65–71	58–59	130–131
RV 2001	Doped spruce	GC and HPLC ($n=7$)	58			58 ± 11		
RV 2006	Doped spruce	GC ($n=11$)	415			418 ± 17		
RA 2017		GC-ECD				371*		
		GC–MS				376*		
		LC–MS				357*		
RV 2004	Doped pine	GC and HPLC ($n=13$)		196			188 ± 27	
RA 2017		GC-FID					113*	
		GC–MS					138*	
		HPLC–UV					134**	
		LC–MS					126*	
RV2005	Doped spruce	HPLC–UV ($n=5$)			221			215 ± 12
		GC ($n=11$)						228 ± 27
RA 2017		GC-ECD						209*
		GC–MS						221*
		HPLC–UV						205*

RV interlaboratory studies on doted milled wood samples, *RA* repeated analysis of stored sample

*Data from one laboratory only (mean, $n=3$)

**Data from another laboratory

treated wood. Sample C was selected for this experiment since it allows comparison of results for the two triazoles and permethrin. During the second series of experiments, 81–88% of the original amount of propiconazole, 70–78% of tebuconazole and 93–94% of permethrin were determined by HPLC–UV using different calibration solutions (obtained contents of the target substances are presented in Table 3).

Again, contrary observations were made in different laboratories, whereby matrix calibration did not affect the results for permethrin. In general, HPLC-analysis of permethrin proved to be more robust than analysis of the two triazoles in both series of experiments (see SD-values in Table 3). This is probably caused by the fact that most interfering signals from matrix components appear for more hydrophilic substances that elute at similar retention times to that of the two investigated triazoles. In fact, one laboratory reported that it was impossible to distinguish tebuconazole from interfering signals. There are certainly fewer interfering signals for permethrin, which elutes later during the chromatographic run.

Reports on background values originating from the matrix samples were not consistent between the laboratories, i.e., due to different separation conditions. Blank values at retention times of all three analytes were observed for some separation conditions, whereas blank values were observed for only selected analytes for other conditions. Some laboratories did not report blank values. The observations differed for matrices A and B.

3.4 Variability of HPLC results

It is assumed that high variability in the results from HPLC analysis was caused by the influence of matrix components. Lower numbers of theoretical plates of HPLC- compared to capillary GC-columns cause lower resolution, i.e., co-elution of analytes and matrix components is more likely in HPLC-procedures than in GC-procedures. This is more relevant for triazoles than for the late-eluting permethrin isomers. Disadvantages of low resolution can be circumvented by using selective detectors like mass spectrometers. In fact, results from LC–MS-analysis fit well with data obtained from GC-analysis.

Another option is to optimize separation conditions. Comparison of results regarding different HPLC columns did not indicate column types that are not suitable for this analysis. As demonstrated in Fig. 2, optimizing the elution conditions offers the potential to improve separation of the analytes from

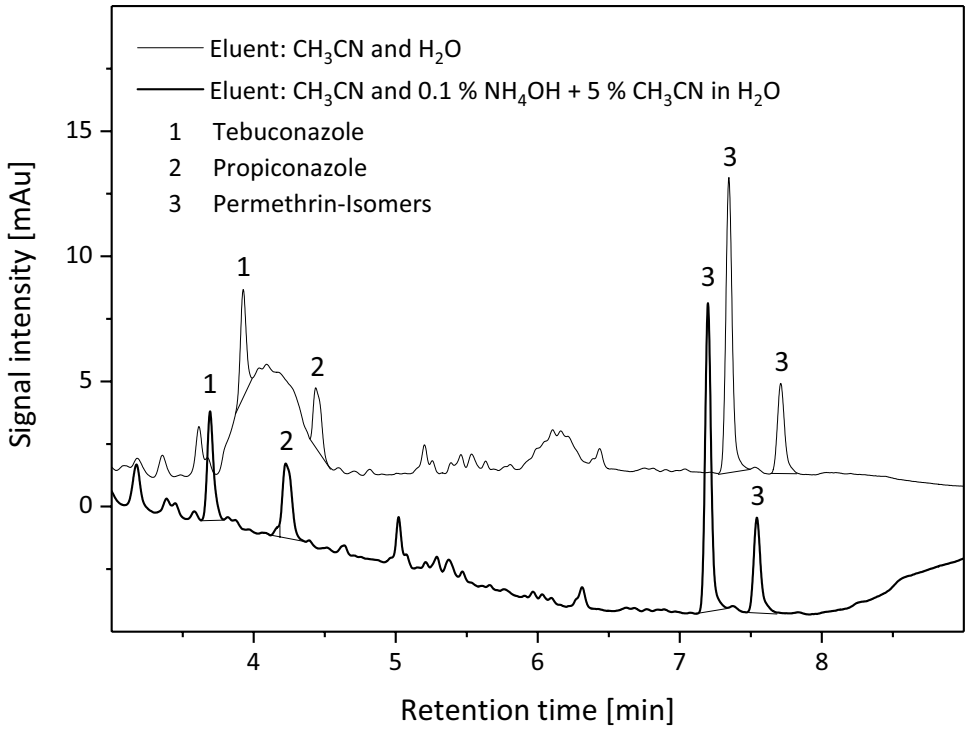

Fig. 2 UHPLC-chromatograms of a methanolic extract from sample C separated by different eluents on a Poroshell C18 column

other components in the wood extract. The analytes were eluted faster, and interfering signals were separated from the signals of the triazoles by using an alkaline eluent. The results were close to the mean values from all laboratories when using acetonitrile (CH_3CN) and 0.1% ammonium (NH_4OH) + 5% CH_3CN in water for gradient elution (UHPLC-UV).

Interference of triazoles and wood components during liquid chromatography of wood extracts was also reported by Miyauchi et al. (2005). They applied clean-up by solid phase extraction on mixed-mode cation exchanger to remove matrix components in methanol extracts from different conifer species (Japanese cedar, Japanese larch, Yeso spruce, Sakhalin fir and Western hemlock) and obtained signals for tebuconazole and cyproconazole that were separated from matrix components. This approach was not tested during this study. Probably, solid phase extraction can also be useful to remove interfering components from other wood species like pine and spruce species that are commonly used in Europe. It has to be decided according to the requirements within laboratories, whether optimizing the chromatographic procedure, use of selective detectors like mass spectrometers or extended sample preparation suits best to handle possible matrix effects.

3.5 Stability of propiconazole, tebuconazole and permethrin in wood

Recovery rates for propiconazole and permethrin in doped samples of milled spruce and tebuconazole in doped samples of pine wood were consistently high in former interlaboratory tests (see Table 3). Usually, these samples were analyzed within a few weeks up to a few months after preparation of the material. The results for repeated analysis of sample C indicate that the analytes were not stable in the milled samples under the given storage conditions (see Table 3). The storage time between the two experimental series was at least 4 months. Repeated analysis of the milled wood samples from the former interlaboratory tests in single laboratories also yielded lower retention than originally observed (see Table 3). It might be that the amounts of triazoles found in this study were effected by fractions that became strongly bound to the wooden matrix as described by Kukowski et al. (2017). This seems to be less relevant for permethrin. Low extractability of strongly bound triazoles can be overcome by more severe extraction conditions as demonstrated by Šťávová et al. (2011) and Kukowski et al. (2017). The amount of a strongly bound fraction probably depends not only on duration and conditions of aging, but also on additional components in the applied wood preservative. This has to be investigated in future experiments.

It is recommended to analyze wood samples as soon as possible after preparation of milled samples.

Because of the lower recoveries for stored milled wood samples, only results from the first series of experiments were considered for interpretation of the analytical results for the aged wood samples. For sample C, which was stored for 1.5 years prior to sample preparation, the concentrations of propiconazole and permethrin were in the range of the

calculated original amounts, whereas the concentration of tebuconazole had slightly decreased. The concentrations of both triazoles decreased in the samples that were already 8 years old, whereas the residual contents were higher for propiconazole than for tebuconazole.

It has to be expected that part of the triazoles was depleted under outdoor exposure of sample B compared to storage conditions for sample A due to emission into wet soil after rain events. Kukowski et al (2017) observed depletion of about 20% of the original amount of tebuconazole in treated wood under outdoor conditions at Hilo (Hawaii) for 6 months, which was mainly related to leaching due to about 1600 mm rain during this experiment. They demonstrated that depletion only occurred in the fraction of loosely bound tebuconazole, whereas the strongly bound fraction remained constant.

In this study, the residual contents for both triazoles tend to be lower in sample B, which has been exposed to soil contact for 6 years, which is also indicated by statistical evaluation (two-sample *t* tests at 95% confidence level) of data from GC analysis and LC–MS analysis of tebuconazole. However, this tendency was not observed by HPLC–UV analysis due to the high variability in the results. See Tables 1 and 2 for the experimental data.

4 Conclusion

In principle, the HPLC and GC methods that have been developed using fresh samples of wood with defined contents of analytes are suitable to determine propiconazole, tebuconazole and permethrin also in aged wood samples. However, recovery rates were observed to be lower for aged wood samples than earlier determined for newly prepared wood samples. More severe extraction conditions can be required if parts of the active substances are strongly bound in treated wood.

Special attention is required for interfering signals if HPLC–UV methods are applied. One option to improve accuracy of HPLC–UV methods—besides application of specific detectors and clean-up by solid phase extraction—is to optimize the eluting gradient to avoid interfering signals. Matrix calibration cannot be recommended for HPLC–UV-analysis. Usually, the untreated wood sample does not originate from the same source as the wood sample that has to be analyzed for preservatives. Wood samples of different origin can cause different interfering signals.

Comparison of HPLC–UV data with results from alternative analytical methods, i.e. either GC- or LC–MS-procedures, can be considered if analytical results are close to limit values for decisions whether specified values are met.

Generally, it is recommended to check recovery rates for any of the applied methods by parallel analysis of wood samples with defined content of the analytes to ensure current suitability of the used equipment for the required analysis.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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