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Journal of Chromatography A, 953 (2002) 199–205

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Analyses of the wood preservative component *N*-cyclohexyl-diazeniumdioxide in impregnated pine sapwood by direct thermal desorption–gas chromatography–mass spectrometry

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Received 28 August 2001; received in revised form 21 January 2002; accepted 1 February 2002

Abstract

Investigations concerning the qualitative and quantitative determination of the organic wood preservative component *N*-cyclohexyl-diazeniumdioxide (HDO) in treated timber were carried out by means of direct thermal desorption–gas chromatography–mass spectrometry (DTD–GC–MS). It could be shown that the identification of HDO in treated pine sapwood (*Pinus sylvestris* L.) is relatively simple using this analytical technique. Quantification of this active ingredient can be carried out using the peak area of the specific mass fragment m/z 114. A calibration curve with a high correlation coefficient was obtained in the range from 40 to 550 mg HDO per kg timber. Furthermore it can be deduced that the results obtained are characterised by an excellent reproducibility with standard deviations ranging from 5 to 10% in general. For the chosen experimental set up a detection limit of 4 mg HDO per kg treated pine sapwood was calculated, although merely 20% of the active ingredient was desorbed.

Keywords: Pine sapwood; Wood preservative; Direct thermal desorption; *N*-Cyclohexyl diazeniumdioxide

1. Introduction

The Biocidal Products Directive (BPD) 98/8/EG [1] of the European Parliament and the Council concerning the placing of Biocidal Products on the market was implemented on 24 May 1998 and it had to be transformed into national legislation within 2 years. According to the BPD the member states can approve a biocidal product when the active ingredients are listed in annex I or Ia of the BPD. The inclusion into the annex is carried out by means of so-called ''data sets''. The data sets include information concerning the physical and chemical properties or ecotoxicological information of the biocide as well as procedures concerning the determination and methods of analysis. In total, 23 product types are recorded from the BPD whereby the main group 2 ''preservatives'' contains disinfectants, antifoulings and the product group ''wood

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0021-9673/02/$ – see front matter
PII: S0021-9673(02)00120-6

preservatives''. Wood preservatives can be divided into waterborne preservatives, organic solvent-based preservatives, creosote and special types like gases, containing various types of biocides like fungicides and/or insecticides. The choice of suitable wood preservative formulations depends on the expected hazard class which is described in the European Standard EN 335-2 (1992) [2]. However, to guarantee the protection of the timber the impregnation has to be carried out in a way that the retention required of the active ingredient(s) must be found in a certain penetration depth according to EN 351-1 (1995) [3]. Therefore, quality control by means of chemical analysis is an essential tool to ensure a proper treatment. The quantitative determination of organic active ingredients in timber represents special problems as these compounds are often present in wood in small concentrations and, moreover, they are fixed. Various active ingredients of wood preservatives, e.g., pentachlorophenol, tebuconazole or permethrin, can be analysed by means of pyrolysis–gas chromatography–mass spectrometry (GC–MS) at Curie temperatures of 600 °C [4]. A special analytical technique for this application is thermal desorption (TD)–GC–MS as used by Karpe et al. [5] to identify volatile organic compound emissions. A similar analytical technique, direct thermal desorption (DTD)–GC–MS, was used by Jüngel et al. [6] for the qualitative determination of *N*-cyclohexyldiazeniumdioxide (HDO) in treated wood. First results concerning a possible quantification of HDO were presented at the annual conference of the International Research Group on Wood Preservation (IRG) in 2001 [7]. The authors could clearly demonstrate the possibility of a definite identification of HDO using the corresponding mass spectra. Furthermore, it was pointed out that the chromatograms contain few signals of wood components, although the matrix ''wood'' consists to approx. 90% of the elements C (50%), O (44%) and H (6%). This phenomenon was explained by the relatively low temperatures applied in the thermal desorption unit.

Based on these studies, systematic investigations were carried out to quantify HDO in impregnated timber using DTD–GC–MS whereby parameters like reproducibility or detection limit were determined. In addition, investigations concerning the thermodesorbable amount were carried out which were compared with results of replicate measurements by means of another analytical technique as described by Wittenzellner et al. [8].

2. Materials and methods

Lamellas were prepared from Pine sapwood (*Pinus sylvestris* L.) with the following dimensions: 8.0 cm×3.0 cm×0.4 cm and their dry mass [9] was determined. Finally, the lamellas were kept in a standard climate [10] at a temperature of 20±1 °C and a relative humidity of 65±3% for conditioning. The conditioned test specimens were impregnated with commercial wood preservative formulations Wolmanit® CX-8 and Wolmanit® CX-SD according DIN EN 113 [11] using a vacuum of 30 min followed by 2 h soaking. Both wood preservatives can be described with regard to their characteristics as waterborne, chromium-free, preventively appearing, $Cu(HDO)_2$-salt containing concentrates, and have a so-called construction supervision approval [12].

Impregnation solutions with concentrations ranging from 0.01 to 1.00% were prepared by dilution of the wood preservative formulations. The actual HDO content in the solutions was determined photometically [8]. On the basis of the parameters: dry mass of the lamella, HDO concentration of the impregnation solution and the actual uptake of impregnation solution, the HDO content of each lamella was calculated separately according to equation:

$$w_W = \frac{c_{W(A)}U + (c_{W(A)} - c_{W(B)}) \cdot (m_T - U)}{m_0}$$

where: w_W is the calculated content of HDO in the treated timber (mg/kg), c_W is the HDO concentration of the impregnation solution before (A) and after (B) impregnation (mg/kg), m_T is the mass of the impregnation solution used for impregnation (g), U is the actual uptake of impregnation solution (g), and m_0 is the dry mass of a certain lamella (g).

The treated test specimens were stored for 4 weeks in a standard climate for fixation. After fixation, each lamella was separately split and milled in a cutting mill type Retsch SM-1 (sieve insert with a hole size of 3 mm). Finally the material was milled again for

further homogenisation in a laboratory mill type IKA MF 10 (sieve insert with a hole size of 2 mm) for approx. 1 min. The wood powder was stored in a standard climate until analysing.

2.1. Analytical equipment and procedure

For the analytical experiments an Agilent 6890 GC (Agilent Technologies, Wilmington, NC, USA) equipped with an Agilent 5973N mass spectrometric detector (Agilent Technologies, Palo Alto, CA, USA) was used. The injection interface was an Optic 2 programmable injector (ATAS International, Veldhoven, The Netherlands) equipped with an DTD Automatic Liner Exchange Unit (ATAS International). A Focus XYZ Sample Processing Robot (ATAS International) performed transportation of liners. The liners have a length of 80 mm and an I.D. of 3.4 mm. The top of the liner has an 11 mm O.D. flange for sealing the liner with a crimp cap. The Agilent 6890 GC instrument was equipped with a HP5-MS (J&W, Folsom, CA, USA) column of 30 m×0.25 mm I.D. Helium 5.0 (Hoekloos, Schiedam, The Netherlands) was used as carrier gas for the system.

For the quantification of HDO in treated timber 10±0.1 mg of $Cu(HDO)_2$ containing wood powder was weighed into the liners, sealed with magnetic crimp caps and placed into the injector, having a start temperature of 45°C. After purging the liner with carrier gas during 30 s the injector was heated with 10 K/s to 200 °C with a desorption time of 60 s. During the first 105 s of the analysis the system pressure was 128 kPa, to perform a high liner flow to perform a good purge and rapid sample transfer to the capillary column. After the desorption time the pressure was set to 70 kPa to perform optimum column flow and programmed to 128 kPa for constant flow conditions. The GC oven temperature started at 50°C. After one min the column was heated with 40 K/min to 250 °C with ramps at 110 °C for 1.5 min and at 140 °C for 3 min. The total run time was approx. 11 min. The mass spectrometer started its run after 2 min and stopped at the end of the GC run, whereby the mass range from 35 to 150 was recorded. The control of the GC–MS system as well as the evaluation of the chromatograms received were carried out by means of Software Enhanced ChemStation G 1701CA (Agilent Technologies).

3. Results and discussion

3.1. Retention time and mass spectra

Fig. 1 illustrates that a sharp signal is recorded in the chromatogram after $t_R = 4.49$ min. From the corresponding mass spectra it can be deduced that this signal represents HDO. The high peak intensity is due to relatively high HDO content in the sapwood. A comparison with previous mass spectra [6] achieved with a Finnigan GCQ clearly illustrates that differences exist only with regard to the relationship of the signal intensity of the mass fragments which might be a result of specific construction differences of both mass spectrometers.

Besides unspecific mass fragments like m/z 39, 41 or 55, the mass spectra of HDO also contain the fragment m/z 114, whereby the formation mechanism of this mass fragment can be explained according to Fig. 2. It is to be expected that $Cu(HDO)_2$ is also to be found in wood as a salt [13] with a crystal structure (I) as described by Klebe et al. [14]. As a result of the thermal energy supplied and in the presence of water (wood moisture) the crystalline $Cu(HDO)_2$ should be transformed into an intermediate compound (II) having a *N*-cyclohexyldiazeniumdioxide structure [15]. A fragmentation with the loss of NO should take place as a result of the bombardment [16,17] by which the mass fragment is formed. The mechanism suggested is also confirmed by results published by Horn et al. [18] who found similar fragments during the Curie-Point-pyrolysis of $Cu(HDO)_2$ crystals. For the reaction step (I) the influence of water could also be confirmed experimentally, whereby the signal intensity increases gradually with increasing wood moisture content. Therefore, all of the quantitative analyses have to be carried out under identical moisture conditions.

3.2. Reproducibility and detection limit

The reproducibility of the chromatographic method described was checked by means of milled material containing different HDO concentrations whereby each concentration level was investigated three times. Fig. 3 shows the mean values and standard deviation calculated on the basis of the peak

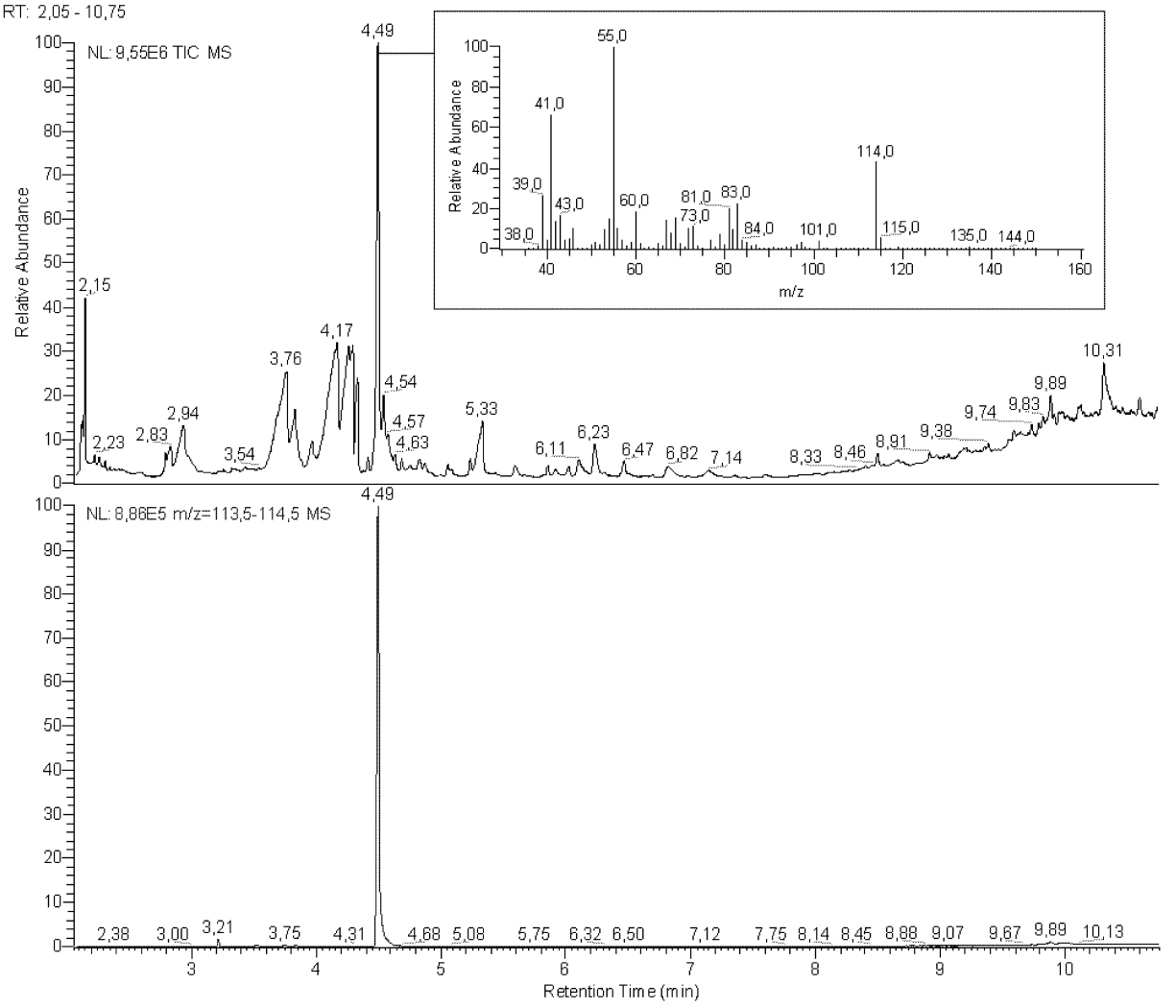

Fig. 1. Pine sapwood (*Pinus sylvestris* L.) treated with Wolmanit® CX-SD using milled material with a content of 553 mg HDO per kg timber. Top: Full scan chromatogram (TIC) and the mass spectra of HDO. Bottom: Selected ion chromatogram for m/z 113.5–114.5.

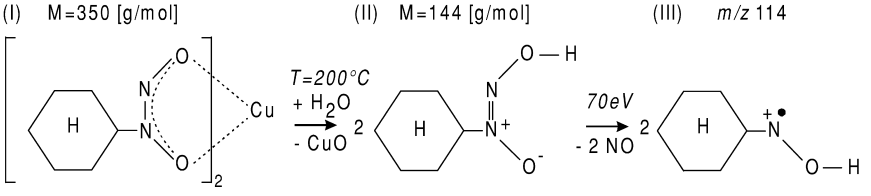

Fig. 2. Hypothesis regarding the origin of the mass fragment m/z 114 in the mass spectra of HDO after thermal desorption–GC–MS of $Cu(HDO)_2$ according to Refs. [13–17].

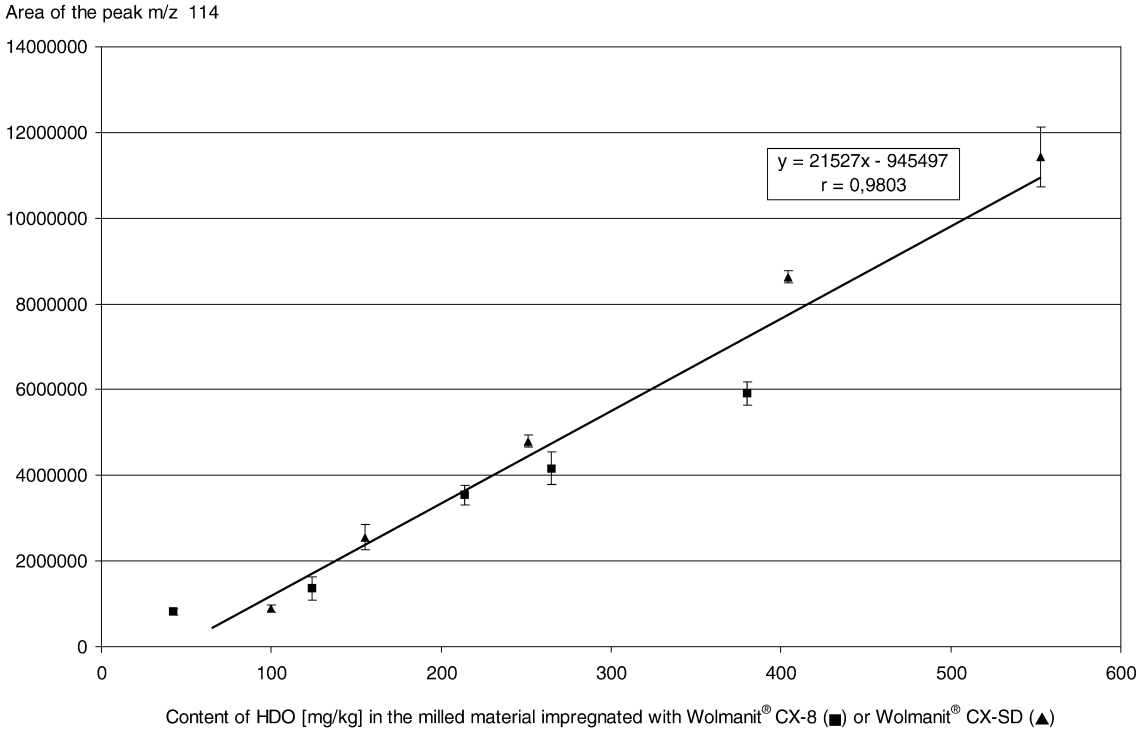

Fig. 3. DTD–GC–MS analyses of HDO in treated pine sapwood (*Pinus sylvestris* L.). Mean values and standard deviations ($n=3$) of the signal areas for the mass fragment m/z 114 using timber impregnated with Wolmanit® CX-8 or Wolmanit® CX-SD depending on the HDO concentration in milled material and the calibration function deduced.

area for the selective mass fragment 114 for the concentration interval 42 to 553 mg/kg. It is worth mentioning that the standard deviation is generally lower than ±10%. In one case a clearly bad value was obtained with $s=\pm 19.9\%$. The calibration curve shows a correlation coefficient of $r=0.9803$.

The determination of the detection limit of this analytical procedure based on nine replicates whereby milled material was used containing 7 mg HDO/kg timber. The calculation was carried out according to the equation:

$$\mathrm{DL}=\frac{s}{\bar{x}}\cdot w_{\mathrm{W}}t_{99\%}=\frac{29\,824}{191\,941}\cdot 7\cdot\frac{\mathrm{mg}}{\mathrm{kg}}\cdot 3.355$$
$$=3.6\cdot\frac{\mathrm{mg}}{\mathrm{kg}}$$

where DL is the detection limit (mg/kg), s is the standard deviation, $\bar{x}$ is the mean value ($n=9$), w_{W} is the content of active ingredient (mg/kg), $t_{99\%}$ is the t-value for $\alpha=0.01$ and $f(n-1)=8$.

The detection limit is 4 mg HDO per kg pine sapwood for the analytical parameters chosen.

3.3. Thermodesorbable amount

The determination of the thermodesorbable amount of HDO was carried out by means of DTD–GC–MS using crystals of $Cu(HDO)_2$, which were dissolved in methylene chloride, and HDO containing milled wood. The concentration of HDO was adjusted in a way that an identical amount of HDO was to be found in the liquid sample as well as in the impregnated timber. Based on the results received a thermodesorbable HDO content of 14% was calculated.

Furthermore, chips with an analytically determined HDO content of 450 mg/kg were stored according to the conditions in the thermal desorption unit in an oven at a temperature of 200 °C for 1 and 2 min, respectively. This thermally pre-treated ma-

Table 1
HDO content in treated pine sapwood (*Pinus sylvestris* L.) in correlation with the duration of thermal treatment and the calculated ratio of the thermal desorption

Series	Thermal treatment of the wooden material	Content of HDO determined by HPLC (mg/kg)	Thermal desorption rate (%)	Qualitative determination using DTD–GC–MS
0	Without	450	–	Positive
1	1 min at 200°C	360	20	Traces
2	2 min at 200°C	328	27	Negative

terial was investigated using HPLC with regard to the remaining HDO concentration in the timber (Table 1). The table clearly illustrates that the HDO content decreased from 450 to 360 mg/kg after a thermal treatment at 200 °C for 1 min corresponding to 80% of the initial concentration. This observation fits well with results obtained by the liquid analysis of dissolved $Cu(HDO)_2$ crystals. The minimally higher thermal desorption rate during storage in an oven can be explained by a further evaporation of HDO during cooling in the dessiccator before analysis. It can also be seen that a prolongation of the thermal treatment leads to a further decline of the HDO concentration. The evaporated gas during the extended cooling off period is not registered in the investigation by means of DTD–GC–MS. From these results it can be deduced that between 15 and 20% of the organic active ingredient have vaporised as a result of the chosen thermal desorption parameters.

In addition to this, parallel DTD–GC–MS investigations were carried out, using thermally pre-treated timber. As expected, the results in Table 1 clearly demonstrate that HDO cannot (or only in traces) be identified after a thermal pre-treatment. This observation is a further indication that the thermodesorbable amount of HDO was transformed quantitatively into the gaseous phase.

4. Conclusions

Within the development of new analytical methods the direct analysis of solids is becoming more and more important. Especially the renunciation of extensive sample preparation does not only reduce the expenditure of work but also in some cases makes an analysis possible at all, or at least minimises possible error sources.

Primarily, a lack exists in the quantitative determination of organic wood preservative components in treated timber. DTD–GC–MS represents an interesting alternative since this technique shows a high sensitivity as well as a high selectivity and at the same time it requires only small amounts of sample material. Therefore, this procedure should be suitable for investigating penetration behaviour of wood preservative components in treated timber and the non-destructive material testing in the context of quality control.

Systematical investigations regarding the quantification of HDO in treated pine sapwood showed that this substance of waterborne wood preservatives could be quantified by means of DTD–GC–MS. During these measurements it could be observed that the performance was excellent for the whole system. For example a series of investigations could be carried out in the course of a continuous 24 h measuring procedure without any problems so that the running time of the equipment is determined by the capacity of the sample rack or of the test design only. However, a limiting factor is to date that no certified impregnated wooden material is available. The sample preparation protocol might be an interim solution since the results achieved showed an acceptable reproducibility and the determined calibration curve resulted in a high correlation coefficient with $r = 0.9803$, although approx. 20% of the HDO were desorbed from the treated pine sapwood.

Acknowledgements

Our sincere thanks to Dr. Wolman GmbH, Sinzheim, for the free supply of wood preservatives. For the HPLC experiments we would like to thank Dr. Wittenzellner, Dr. Wolman GmbH.

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