Application Note No. 051

Determination of N-cyclohexyl-diazeniumdioxide (HDO) containing compounds in treated wood using GC-MS

by
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ABSTRACT

Beside the biological effectiveness the approval of a chemical wood preservative requires also techniques for the analytical determination of active ingredients in different matrices. Fulfilling of the last requirement is particularly difficult in the case of impregnated timber treated with wood preservatives containing organic compounds.
This paper describes a procedure for the determination of the organic ingredient N-cyclohexyl-diazeniumdioxide (HDO) in solid phases using gas chromatography coupled with mass spectrometry (GC-MS) in connection with a previous thermal desorption step.
For this powdered samples are placed in a glass tube. Then the tube is reinserted into the thermal desorption unit which is placed in the GC-oven and directly connected with the capillary column. Afterwards the sample was quickly heated up to 200°C. The resulting gas mixture is pushed onto the column and the separation of the gas components took place. The single components could be identified by means of the retention time and the mass spectrum. A quantitative determination seems to be possible by means of the intensity of the signals.
The suitability and reproducibility of this method of the determination of HDO were tested successfully by analysing a number of impregnated wood specimens treated with different formulations containing HDO.

Key words: GC-MS, thermal desorption, analysis, N-cyclohexyl-diazeniumdioxide (HDO), wood preservative, impregnated wood

1 INTRODUCTION

The conversion of the Biocidal Products Directive 98/8/EC (BPD) requires also an environmental risk assessment for impregnated timber. The analytical determination of wood preservative components in different matrices is an important tool for any such assessment. At the moment, however, there are deficits in the availability of suitable methods of analysis for the detection of organic wood preservative components in solids, for example wood.
The gas chromatography coupled with different detection systems represents a widespread method, which was used successfully for the determination of organic components in treated wood (FERLAZZO 1999). The execution of this procedure, however, requires often an extensive sample preparation, like an extraction of impregnated wood.
A direct method represents the pyrolisis-GC-MS (HORN and MARUTZKI 1994). This technique is particularly remarkable: despite the high temperatures (700 degree) thermally unstable substances can be analysed. A disadvantage is that beside the substances of interest also numerous pyrolysis products of the wood should be pushed onto the GC-column. As a result of this the ratio of the signal to the background can be worse. It is to be assumed that the content of pyrolisis products of the wood should be decrease when this investigation is carried out at lower temperatures (thermodesorption). Therefore on the basis of thermodesorption - GC-MS (KARPE

et al. 1995), the possibility of a determination of the wood preservative component HDO have been investigated.

2 MATERIAL AND METHODS

2.1 MATERIAL

The investigations were carried out using water-soluble K-HDO and treated Pinus-sapwood. The wood specimens were impregnated with K-HDO or Cu-HDO based WOLMANIT® CX-products.

2.2 DESCRIPTION OF THE TECHNICAL EQUIPMENT

Figure 1 shows the technical equipment used

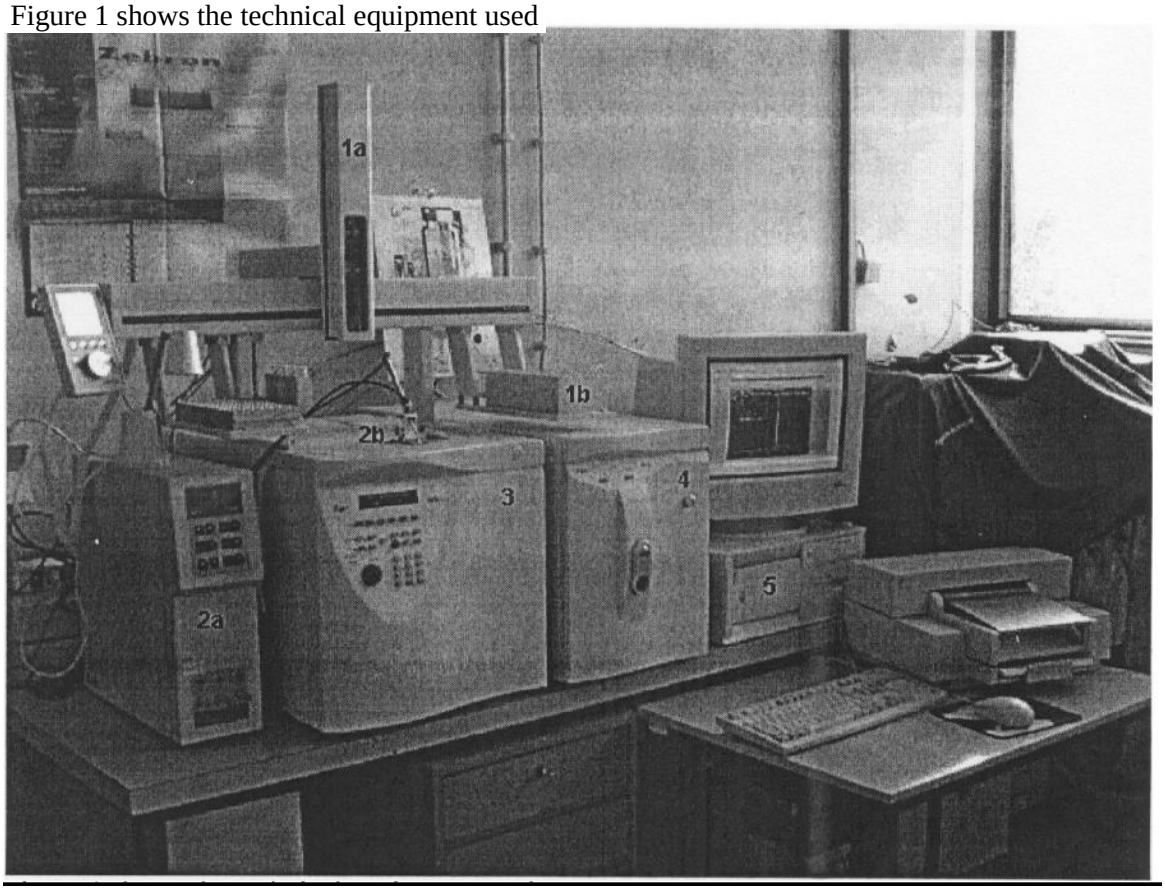

Figure 1: technical device consisting of 1a: automatic sampler (ATAS); 1b: sample rack with vials; 2a: control element of the thermodesorption-unit; 2b: thermodesorber; 3: GC (Finnigan); 4: MS (Finnigan); 5: Computer including GC-MS software

2.3 SAMPLE PREPARATION OF TIMBER

The wood specimens were splitted and a so called "Retschmill" was used to produce wood chips. The size of chips was limited by means of a sieve attachment with a mesh size of 3 mm. During this procedure a homogenisation of the sample material took place.

Up to 20 mg of the powdered samples are placed in a vial. Then the tube is reinserted into the thermal desorption unit which is placed in the GC-oven and directly connected with the capillary column. Afterwards the sample was during few seconds heated up to 200°C. A part of the resulting gas mixture is pressed onto the column of the GC and the separation and fragmentation of the gas components took place. The parameters for investigation are shown in table 1.

Table 1: Settings of the GC-MS methods

Instrument Settings				
Ionisation Mode:			EI (+)	
Column type:			SGE BPX 35	
MS-method				
Mass spectroscopy:			Ion Trap	
Seconds per Scan:			0.50 seconds	
Source Temp:			200 °C	
Transfer Line:			275 °C	
Start Time:			1.00 minutes	
Micro Scans:			5	
Scan Mode:			Fullscan First Mass: 35 Last Mass: 150	
GC Method – Oven temperature program:				
Initial value:			50.00 °C	
Initial time:			0.50 minutes	
Ramp	Rate [°C/ min]	Final [degrees]	Hold [minutes]	Total [minutes]
1	40.00	120.00	0.50	2.75
2	40.00	160.00	1.50	5.25
3	40.00	270.00	1.00	9.00
4	0.00	270.00	0.00	9.00
GC Method – Injector pressure program:				
Initial value:			8.00 psi	
Initial time:			4.00 minutes	
Ramp	Rate [psi/ min]	Final [psi]	Hold [minutes]	Total [minutes]
1	2.00	16.00	0.00	8.00
2	6.00	24.00	1.00	10.33
3	4.00	30.00	2.00	13.83
4	0.00	30.00	0.00	13.83

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3 RESULTS

Figure 2 shows the chromatogram obtained for K-HDO dissolved in water. The signal in the chromatogram after the retention time of 03:48 minutes should be HDO because this solution contained only HDO as organic component. An indication for this theory is the mass spectrum added. It is to emphasise, that the fragments of HDO can be derived according usual disintegration rules (HÜBSCHMANN 1996). Identical results were received after investigations of solutions containing Cu-HDO as well as crystals of K-HDO and Cu-HDO.

General a lot of signals were obtained in the case of investigations of wood. These signals result from the desorption of substances contained in the wood. Very small signals could be detected for untreated wood around the retention time of HDO. The corresponding mass spectra were not identically to the mass spectrum of HDO.

The chromatogram of K-HDO treated sample is shown in figure 3. It is to be seen, that a clear signal exist at the retention time of 03:47 minutes. The evaluation of the corresponding mass spectrum allows the conclusion that this substance is definitely HDO (see the mass spectrum in figure 2).

Identical results were also obtained for wood treated with Wolmanit CX-formulations (see figures 4 and 5). A comparison of both chromatograms shows that an increase of the concentration for HDO in wood leads to an increase of the intensity of the signal for HDO.

From these observations can be deduced, that a quantitative detection of HDO should be possible. Furthermore can be assumed that the detection limit of HDO in treated timber is approx. 50 ppm HDO.

4 OUTLOOK

Based on the previous results principally the investigations have to be concentrated on the following topics:

- Use of this procedure for different wood species
- Quantitative determination of HDO (calibration)
- Testing the suitability of this method for determination of HDO in different matrices
- Adaptation of this procedure on other organic active ingredients

5 REFERENCES

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KARPE, P.; KIRCHNER, S.; ROUXEL, P. 1995. Thermal desorption-gas chromatography-mass spectrometry-flame ionization detection-sniffer multi-coupling: A device for the determination of odorous volatile organic compounds in air. Journal of Chromatography A 708, 105-114.

Chromatogram Plot

Comment:	2µl K-HDO solution containing 500 ppm HDO on glass wool
Scan No:	90
Retention Time:	03:48
RIC:	6409442
Mass Range:	36- 149
Plotted:	1 to 112
Range:	1 to 112
100% =	6409442

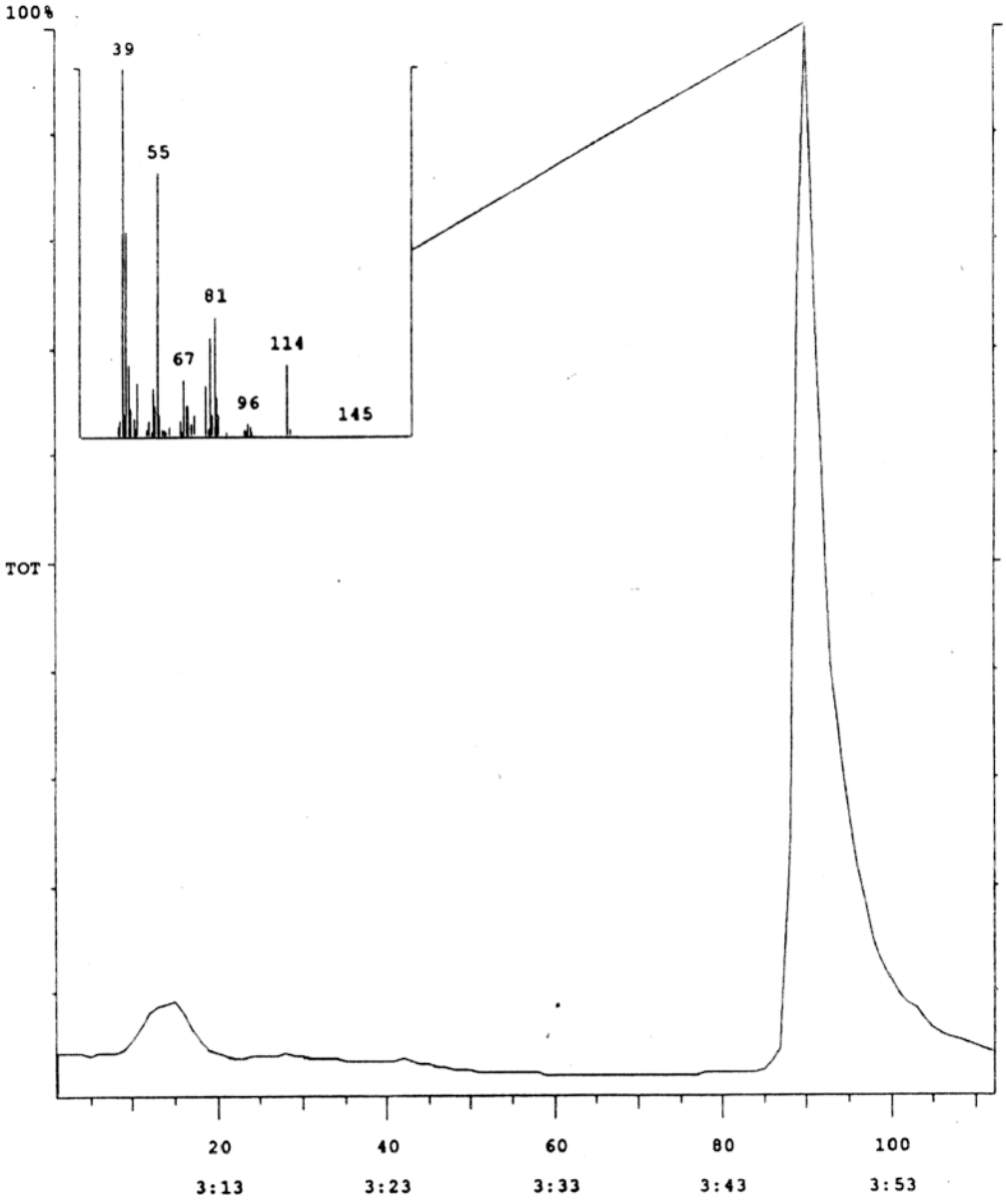

Figure 2: Chromatogram and mass spectrum of K-HDO dissolved in water

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Chromatogram Plot

Comment: EN 113 specimen treated with K-HDO (initial retention approx. 6kg/m^3)
Scan No: 329
Retention Time: 03:47
RIC: 9823420
Mass Range: 35 –150
Plotted: 100 to 500
Range: 1 to 508
100%= 9823420

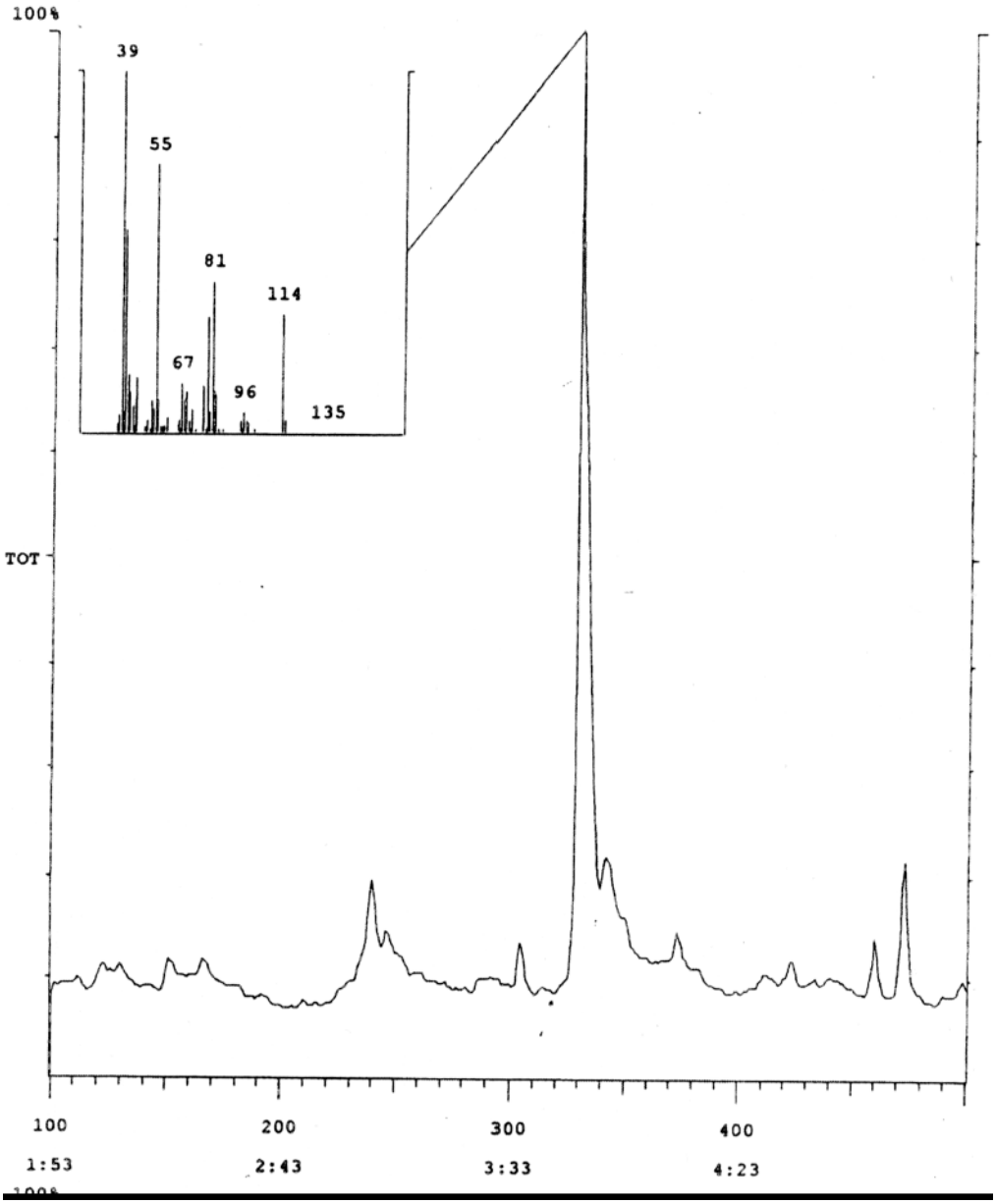

Figure 3: Chromatogram and mass spectrum of impregnated timber treated with K-HDO

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Chromatogram Plot

Comment: Timber treated with Cu-HDO; containing 93 ppm HDO; sample mass 15.8 mg
Scan No: 332
Retention Time: 03:49
RIC: 4761835
Mass Range: 35 –150
Plotted: 50 to 500
Range: 1 to 609
100%= 10827050

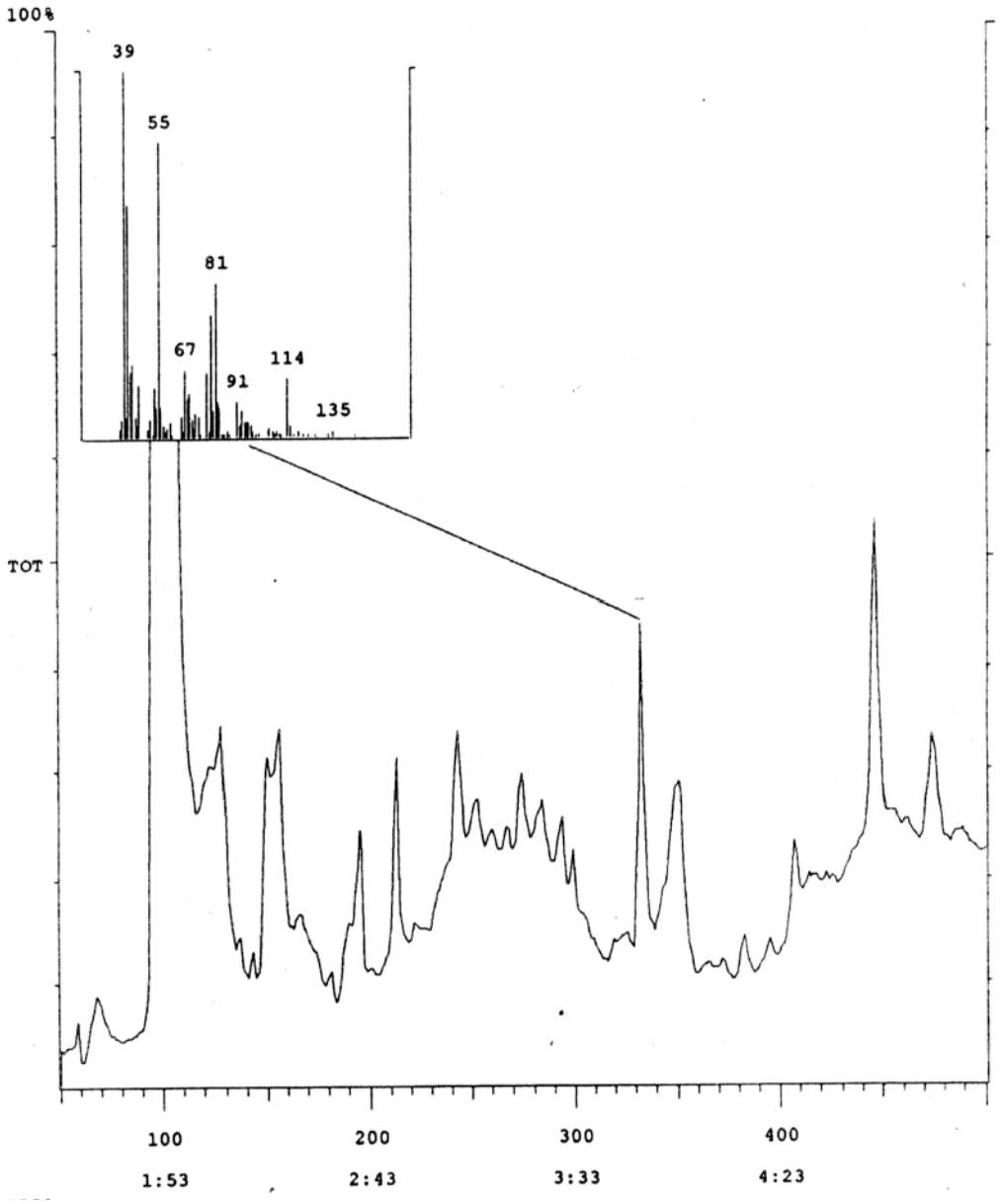

Figure 4: Chromatogram and mass spectrum of wood treated with a Wolmanit® CX-formulation and a initial retention of 93 ppm HDO in the specimen

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Chromatogram Plot

Comment:	Timber treated with Cu-HDO; containing 233ppm HDO; sample mass 15.1 mg
Scan No:	249
Retention Time:	03:47
RIC:	14350520
Mass Range:	35 –150 50
Plotted:	to 500 1 to
Range:	632
100%=	27857290

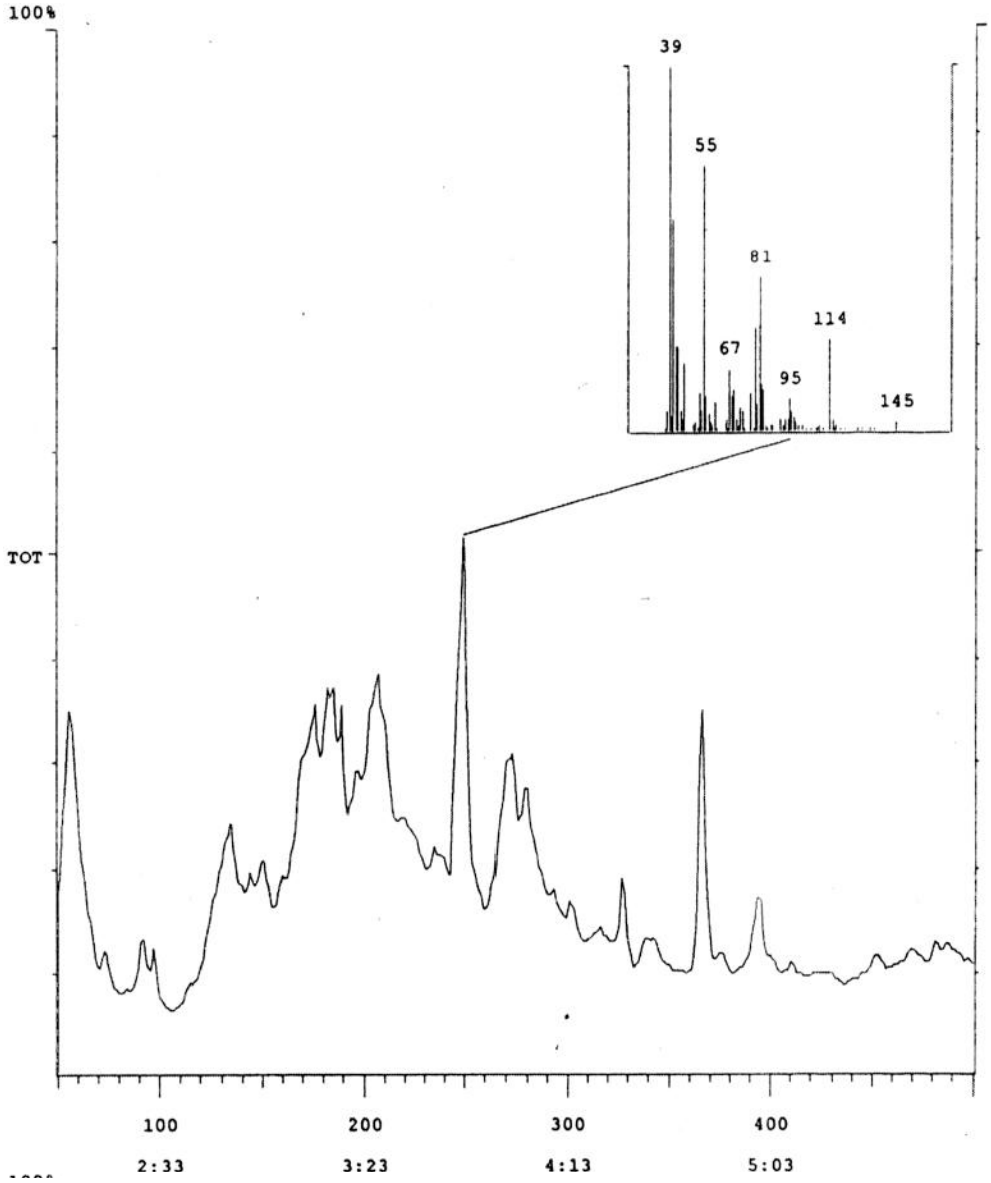

Figure 5: Chromatogram and mass spectrum of wood treated with a Wolmanit® CX-formulation and a initial retention of 233 ppm HDO in the specimen

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