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Short communication

Coupling of thermal desorption in modified closeable sampling columns with wide-bore capillary gas chromatography and mass spectrometric detection

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Abstract

In contrast to usability of Curie-point pyrolysis at 700°C directly attached to gas chromatography–mass spectrometry (GC–MS) for determination of organic wood preservatives in waste wood samples the investigation method reported here consists of thermal desorption at temperatures about 260°C in connection with GC–MS for peak identification or GC with flame ionization detection for quantitative analyses. So-called "modified closeable sampling columns" are used as batch-reactor in thermal desorption experiments. Desorbed vapours can be introduced on capillary columns without sample discrimination and without a disturbing lost of resolution. In this manner a lot of individual polycyclic aromatic hydrocarbons were determinated in waste wood samples, especially in railway sleepers.

Keywords: Thermal desorption; Closeable sampling columns; Capillary GC; GC–MS; Wood; Characterization of waste wood; Sample preparation; Polynuclear aromatic hydrocarbons

1. Introduction

The use of creosote as a wood preservative is well known. Importance of tar-oil, resp. creosote, for wood preservation is reported by Schulz [1]. The behaviour and change of chemical composition of tar-oil in beech sleepers by ageing are investigated by Osusky and Bosshard [2]. But there are toxic and environmental problems caused by creosote during and after its application.

A special case of creosote treated waste wood are railway sleepers which came from closed brown coal open-casts in abundance. Therefore can be of interest the development of a practicable method for wood sample screening tests and for determination of polycyclic aromatic hydrocarbons (PAHs) in tar-oil treated railway sleepers.

Schaefer and Püttmann [3] applied a micro-scale thermodesorption–capillary gas chromatography combination to study the hydrocarbon distribution in coals. A similar method should be useful also to investigate wood samples. However, Faix et al. [4] studied the thermal degradation of wood at 450°C and reported the results of analysis of wood degradation products by GC–MS. Gray et al. [5] have shown that pyrolysis of wood-derived material at 320°C yields in the main acetic acid (2.9% of initial mass), 1-hydroxy-2-propanone (2.7%), furfural (0.8%) and guajacols (1.7%). Usability of Curie-point pyrolysis at 700°C directly attached to GC–MS for determination of organic wood preservatives in waste wood samples was described by Horn and Marutzky [6].

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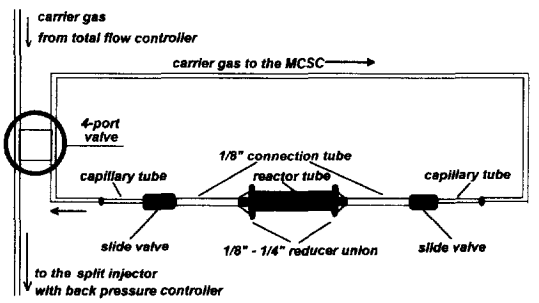

Fig. 1. Modified closeable sampling column (MCSC) and gas flow scheme for sample introduction into open tubular column.

In contrast to [6] and with regard to [5] the investigation method reported here consists of thermal desorption at temperatures preferable about 220–300°C in connection with GC and GC–MS. Closeable sampling columns developed for GC analysis of petrochemical vapour samples [7] were modified for taking up solid samples and are used as batch-reactor for thermal desorption experiments.

Waste wood shavings can put into such a "modified closeable sampling column" (MCSC). After heating up to an adjusted temperature volatile components are desorbed from the waste wood sample and the hot MCSC is connected as a sampling loop with a heated gas sampling valve of a gas chromatograph. Then analysis of desorbed vapours is carried out. In this manner characterization of preserved and non-treated wood should be possible.

2. Experimental

2.1. Modified closeable sampling column (MCSC)

Non-uniformity of wood material requires a sample size of about 50 mg. Therefore our closeable sampling columns [7], developed for vapour samples, were modified in their middle part by a "reactor tube" having an additional volume of 1.3 ml, a length of 80 mm and an internal diameter of 4.6 mm. It appears from Fig. 1 that such a "modified closeable sampling column" (MCSC) consists of the stainless steel "reactor tube" with two 1/4 in. to 1/8 in. (1 in.=2.54 cm) reducing unions, two stainless steel "connection tubes" and two dead volume free "slide valves" at both ends. The slide valves merge into short capillary tubes.

The middle part of the MSCS acts as desorber vessel or reactor tube. Weighted wood shavings of about 50 mg are put into this reactor tube which is screwed on the other parts of the MCSC by means of the reducing unions at both ends. At room temperature gas volume of such MCSC containing the wood sample is purged with an argon flow and closed by its slide valves.

2.2. Thermal desorption experiments

As shown in Fig. 1 the middle part of MCSC is put into isolated oven (size: 100×80×80 mm). Then the oven is heated up in 10 min to an adjusted temperature by a hot air stream. Temperatures between 100°C and 500°C are possible. In thermal desorption experiments reported here temperatures up to 300°C (preferably 260°C) and 4 min isothermal period were used.

2.3. Sample introduction for GC analysis

Immediately after heating period the hot MCSC is connected as sampling loop with a heated gas sampling valve of the gas chromatograph. A portable device, consisting of connection lines and the sampling valve with heating facilities, proofs well for sample introduction from the MCSC on different gas chromatographs as GC–MSD and GC–flame ionization detection (FID). Because the vapours from the MCSC are diluted by carrier gas to a volume larger than 3 ml, split mode sample introduction and a minimum of cold-trapping for band reconcentration which was achieved by a low start temperature (30°C for 1 min) and a steep temperature increase (30°C/min up to 60°C) were applied. These conditions yielded already after retention times of 4 min good resolved peaks with peak widths in typical range (smaller than 0.1 min).

2.4. GC and GC–MS analysis

GC and GC–MS conditions are given in Table 1. MS detection for peak identification requires a narrow-bore column and a low flow rate. Discrepancy to large sample volume of thermal de-

Table 1
GC analysis conditions

Fused silica open tubular column		Column length: 24 m, I.D.: 0.32 mm, film thickness: 1,0 μm, Crosslinked Polymethylphenyl Siloxane (SE-54),column "SQ-J 165" was laboratory made
	GC–MS	GC column is downstream additional connected with a restriction column of 12 m length and 0.2 mm I.D. (fused silica HP Ultra2, SE-54; Hewlett-Packard)
Carrier gas	GC–FID	Inlet pressure: 20 kPa H_2, constant flow "off", carrier gas velocity at 30°C: 26.6 cm/s
	GC–MS	Inlet pressure: 110 kPa He, constant flow "off", carrier gas velocity at 30°C: 53.7 cm/s
Temperature program		30°C, 1 min isotherm, rate 30°C/min up to 60°C, then 5°C/min up to 150°C, 8°C/min up to 280°C and 15 min isotherm hold (run time: 51.25 min)
Sample introduction		Modified closeable sampling column "MCSC" in connection with a heated Valco 6-port valve and downstream located split injector at 250°C, split mode, split ratio 1:10
Detection:		Flame ionisation detector at 300°C, transfer line to MS and ion source at 280°C, mass range: 25–500 *m/z*, threshold: 500
	GC–FID	GC 5890 II, Integrator 3396B (Hewlett-Packard)
	Data system	Apex, version 2.11 (Autochrom/ESWE Gera)
	GC–MS	GC 5890 II with MSD 5971A (Hewlett-Packard)
	Data system	ChemStation G1030A (Hewlett-Packard)

sorbed components can be avoided by coupling a 0.32 mm wide-bore thick film open tubular column with a 0.20 mm narrow-bore column (details see GC analysis conditions, Table 1). For that use of "one-ferrule connector" (Chrompack 4780) has been proved very worthwhile. The 0.20 mm column was also the transfer line into the ion source of the mass-selective detector (Hewlett-Packard 5971A). GC–MS peak identification was performed in usual manner.

Quantitative determination of PAHs is made on a GC system (Hewlett-Packard 5890 II) which is equipped with FID. Analyses were external calibrated by PAH solutions (20 mg of each component/100 ml toluene). In preserved wood samples individual PAH are found in concentrations between 0.5 and 160 μg related to 1 g wood.

3. Results and discussion

3.1. Modified closeable sampling column (MCSC)

The MCSC is well suitable as "batch reactor" or vessel for thermal desorption experiments in coupling with GC–FID or GC–MSD. Thermal desorption experiments up to 500°C are possible, but careful cleaning of the MCSC and connection lines is necessary to avoid memory effects and ghost peaks. Tightness of slide valves and unions must be checked before each using period by a hydrogen pressure of 700 kPa in water bath. Stainless steel reducing unions have a sufficient life-time for experiment series.

3.2. Thermal desorption experiments

Wood samples can be characterized by desorption experiments at optimal temperatures between 220°C and 300°C. After heating up to the adjusted temperature an isothermal period of 4 min at 260°C gives the best results. At 300°C and at higher temperatures wood degradation preponderates the thermal desorption. Sample size of 50 mg is the minimum with regard to the non-uniformity of wood material.

3.3. GC–MS identification

If sampling procedure is followed exactly, retention times are reproduced precisely. An average standard deviation for retention times of 0.18% was calculated from 325 values of 25 components determinated by GC–MS analyses. The precision of retention times is sufficiently for transfer of MS identification results to other GC analyses.

More than 15 compounds of wood degradation and 12 individual PAH are identified. Selected results of GC–MS are listed in Table 2.

Table 2
Components identified by GC–MS

Component	Retention Time (min)	R.S.D. (%)	Number of runs
Methylfuran	5.86	0.17	(8)
Crotonaldehyde	6.86	0.39	(5)
2,3-Pentanedione	7.70	0.35	(4)
2,5-Dimethylfuran	8.02	0.30	(11)
Toluene	9.82	0.33	(10)
Furfural	11.84	0.27	(8)
Ethylbenzene	12.86	0.16	(4)
α-Pinene	15.47	0.24	(13)
Camphene	16.09	0.20	(6)
5-Methylfurfural	16.28	0.11	(8)
4-Methoxyphenol	20.79	0.17	(22)
2-Methoxy-4-methylphenol	23.98	0.15	(21)
Naphthalene	24.20	0.15	(24)
2-Methylnaphthalene	27.10	0.16	(17)
1-Methylnaphthalene	27.56	0.16	(17)
2,6-Dimethoxyphenol	27.85	0.15	(14)
Trimethoxybenzene	29.91	0.07	(6)
Acenaphthene	31.38	0.11	(16)
Dibenzofuran	31.92	0.09	(18)
Fluorene	33.19	0.09	(22)
4-Methyldibenzofuran	34.04	0.09	(4)
Phenanthrene	36.60	0.09	(21)
Anthracene	36.76	0.09	(21)
Fluoranthene	41.52	0.03	(12)
Pyrene	42.75	0.14	(13)

Retention times with relative standard deviations (R.S.D.) obtained by using of modified closeable sampling columns for GC–MS analyses of wood desorbates.

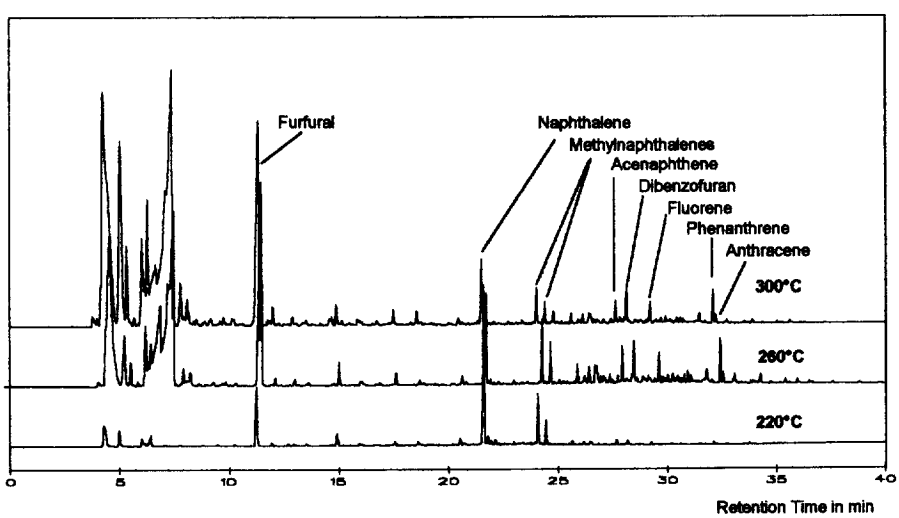

Fig. 2. Chromatograms of thermal desorbed vapours obtained at different temperatures from preservated beech-wood (GC conditions see Table 1).

3.4. Quantitative GC analysis

Because quantitative analyses with FID are better to calibrate than with MS detection, GC–FID was used. Quantitative determination of individual PAHs was performed by external calibration.

Sample introduction of large vapour volumes from the MCSC is connected with a perceptible lost of separation efficiency in range of short retention times. Therefore low boiling components of wood degradation which eluted before 2,5-dimethylfuran could not be determinated by reason of peak overlapping at applied analysis conditions. Components of interest in investigation of wood preservatives especially PAHs elute clearly later (see also Table 2). Chromatograms in Fig. 2 show the different formation of wood degradation products and of PAH in thermal desorption experiments at 220°C, 260°C and 300°C for samples of preserved beech-sleeper.

Use of the MCSC and following of proved introduction procedure peak resolution R_s for pairs of PAHs is founded 6–10% lower compared with automated syringe injection of liquid samples (Table 3). This resolution is sufficiently for peak quantification.

In this way samples of non-treated beech-wood were investigated at desorption temperatures of 100, 140, 180, 220, 260 and 300°C. Related to vapour formation at 300°C equal 100% a vapour formation of 1.2–2.5% was found for temperatures lower than 200°C and all components had retention times lower than 20 min. Increasing formation of wood degradation products is clearly at 220°C (14%) and at 260°C (69%).

Thermal desorption at 260°C of preserved oak-wood and beech-wood railway sleepers was investigated. Contents of individual PAHs were found by GC–FID analyses in concentrations between 0.5 μg (fluoranthene in oak sleeper) and 160 μg (naphthalene in oak sleeper) related to 1 g wood. Results are shown in Fig. 3. Compared with beech sleeper samples naphthalene, methylnaphthalenes and acenaphthene have higher contents in oak sleepers. Dibenzofuran, fluorene, phenanthrene, anthracene and fluoranthene behave contrarily.

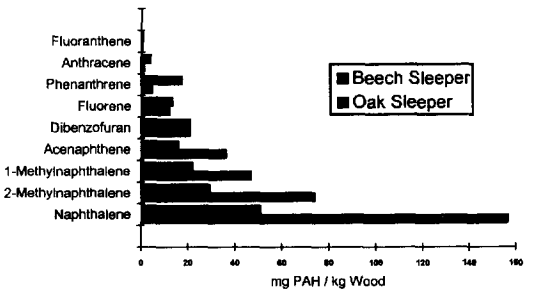

Fig. 3. Individual PAHs thermal desorbed at 260°C from beech and oak railway sleepers and determinated by GC–FID analyses.

4. Conclusion

The test results presented here have shown that different wood species, as preserved as non-treated wood samples, are well distinguishable in this way. Nevertheless interpretation of several results is difficult, can be questionably and further studies will be required to define behaviour of wood at thermal stress conditions. Experiments suggested that a deficient reproducibility is largely due to non-uniformity of wood material.

In summary, the results demonstrate the utility of

Table 3
Resolution R_s of peak pairs obtained by MCSC introduction of vapour samples in comparison to resolution R_s by automated syringe injection of a PAH solution

Peak pair	Syringe injection R_s (R.S.D.)	MCSC R_s (R.S.D.)
2-Methylnaphthalene/1-Methylnaphthalene	4.5 (1.2%)	4.6 (3.7%)
Acenaphthene/Dibenzofuran	6.1 (1.3%)	5.5 (5.5%)
Dibenzofuran/Fluorene	13.5 (1.2%)	12.3 (5.0%)
Phenanthrene/Anthracene	1.7 (1.2%)	1.6 (7.4%)

Mean values of R_s and relative standard deviations (R.S.D.) were obtained by ninefold (syringe injected) and sixfold (MCSC introduced) repeated GC analyses (Conditions see Table 1).

the MCSC, for thermal desorption experiments in coupling with GC, resp. GC–MS analysis.

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