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Separation of phenols and aromatic hydrocarbons from biomass tar using aminopropylsilane normal-phase liquid chromatography

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ABSTRACT

A quantitative procedure for the determination of selected phenols and aromatic hydrocarbons in biomass tar is described. Solid-phase extraction (SPE) through columns of amino-bonded silica stationary phase was used to separate tar samples into two fractions. These fractions were subjected to capillary gas chromatography using a DB-1 fused-silica column and a flame ionization detector. The efficiency of the method was determined by the use of synthetic and spiked tar samples. Excellent reproducibility and high recoveries were obtained for most of the target compounds. Compared with the traditional liquid–liquid extraction technique, the SPE technique eliminates the problems involved and provides higher overall recoveries in a shorter time.

INTRODUCTION

The production of fuel gases by pyrolysis and gasification of biomass for heating purposes and electricity generation are usually accompanied by the formation of various amounts of tar by-products which must be reduced prior to use. Tar reduction for these applications is usually accomplished by thermal and catalytic cracking or by cyclones in combination with wet or dry cleaning systems. The development of new analytical procedures for the determination of individual tar compounds is important in order to control operational parameters at gasification units and for monitoring emissions from full-scale gasifier plants, since several of the tar components have a strong environmental impact owing to their mutagenic and carcinogenic character. Various methods for the characterization of tar matrices have been published. Many of them are based on combinations of the following techniques: high-performance liquid chromatography (HPLC) [1–6], open-column liquid chromatography [4,8,9], capillary column gas chromatography (GC) [1,5,7–9], GC–mass spectrometry (MS) [1,5,6,8,10], solvent fractionation [5,7,8], liquid–liquid extraction (LLE) [1,4,6,8,9], ^{1}H NMR [6,9,12], ^{13}C NMR [6,12], MS–MS [11] and Fourier transform IR spectrometry [10]. The chemical composition of biomass tar varies, depending on the operational conditions, but it is generally very complex and can contain several hundred organic compounds belonging to many chemical classes. Owing to this complexity, a prefrac-

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tionation of the crude tar sample is a common starting point before detailed GC analysis is attempted.

Two conventionally used techniques for prefractionation are LLE and HPLC. These techniques, however, suffer from some disadvantages. Thus HPLC, successfully used in many applications, consumes too large solvent volumes to be useful for a rapid tar analysis method, and LLE when applied to tar samples is associated with the formation of emulsions and problems with the location of the phase boundary. In an attempt to overcome these problems, a quantitative analytical procedure was devised, based on capillary GC following prefractionation by solid-phase extraction (SPE) using micro columns, commercially packed with an amino-bonded silica phase. This technique allows the rapid determination of selected components present in biomass tar formed at high temperatures ($\geqslant 700°C$). To the best of our knowledge, the SPE technique using an amino-bonded sorbent has not previously been employed for this purpose, although amino phase columns have been successfully applied in the HPLC separation of coal-derived tar compounds into aromatic ring classes [3,7].

EXPERIMENTAL

Reagents and materials

Neutral aromatic reference compounds, dichloromethane, sodium sulphate and sulphuric acid were obtained from Merck (Darmstadt, F.R.G). SPE-NH_2 disposable extraction columns (100 mg packing, 40 μm, 60 Å) and 2-propanol were purchased from J. T. Baker (Phillipsburg, NJ, U.S.A.). N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) was obtained from Supelco (Bellefonte, PA, U.S.A.). All phenolic reference compounds except 3,5-di-*tert.*-butylphenol and 2,6-di-*tert.*-butyl-4-methylphenol (Fluka, Buchs, Switzerland) were purchased from PolyScience (Niles, IL, U.S.A.). 4-Ethoxyphenol and 2-bromonaphthalene used as internal standards were obtained from Aldrich-Chemie (Steinheim am Albuch, F.R.G.) and Merck, respectively. All compounds and solvents were of very high purity (mostly >99%) and used as received after being tested in blank procedures.

Gas chromatography and gas chromatography–mass spectrometry

Product analyses were carried out with a modified Packard Model 427 gas chromatograph (split injection) equipped with a flame ionization detector operated at 300°C. Separations were achieved on fused-silica capillary column (30 m × 0.25 mm I.D.) coated with 0.25-μm bonded and cross-linked DB-1 phase (J & W Scientific, Rancho Cordova, CA, U.S.A.). The column inlet pressure was 300 kPa using helium as a carrier gas. The splitting ratio was about 1:50. The injector temperature was 280°C. The oven temperature was programmed from 100 to 300°C at 5°C/min for the analysis of silylated phenols and at 8°C/min for aromatic hydrocarbons. Peak areas were measured with a Shimadzu (Kyoto, Japan) C-R4 A integrator. Two internal standards were used, *p*-ethoxyphenol for phenols and 2-bromonaphthalene for the aromatic compounds. The initial target compound identity was confirmed by GC–MS with subsequent quantitative GC runs based on comparison with retention times relative to those of the internal standards. Relative response factors (*RF*) for all target analytes were calculated from the equation $RF = A(\text{s})C(\text{is})/A(\text{is})C(\text{s})$, where $A(\text{s})$ is the area of the sample peak, $C(\text{is})$ the amount of internal standard added, $A(\text{is})$ the area of the

internal standard peak and $C(s)$ the amount of sample. Electron impact (EI) mass spectra were acquired with a Finnigan MAT 4500 quadrupole instrument at 70 eV, scanning from 40 to 300 u at 0.95 s per scan. The instrument was connected with an Incos 50 data system and a Varian Series 3700 gas chromatograph equipped with a fused-silica capillary column (30 m × 0.25 mm I.D.) coated with 0.25-μm DB-5 using helium as the carrier gas. The oven temperature was programmed at 5°C/min from 80 to 280°C with a 5-min final hold time.

Preparation of samples

Biomass tar was taken from a laboratory research pyrolysis unit operating at 900°C in the absence of a catalyst. The pyrolysis gas was quenched by passing it through a water condenser and a pair of cryogenic traps containing dry-ice–acetone (−81°C) and liquid nitrogen (−195°C) connected in series. The collected tarry aqueous mixture was washed from the condenser and traps with dichloromethane and small volumes of acetone. The washings were transferred into a separating funnel and the organic phase was run off and retained. The aqueous phase was acidified to pH 5 (sulphuric acid) and partitioned with dichloromethane. The organic phase and the combined dichloromethane extracts were dried by passing them through an anhydrous sodium sulphate column, quantitatively transferred into a volumetric flask and diluted to volume with dichloromethane. The total tar sample thus obtained was stored in a refrigerator until it was used.

Synthetic samples were prepared in dichloromethane from eighteen authentic compounds at three concentration levels as follows: synthetic sample 1 = 1.909 mg/ml (86–123 μg of each compound); synthetic sample 2 = 9.672 mg/ml (428–617 μg of each compound); and synthetic sample 3 = 32.060 mg/ml (1.22–2.47 mg of each compound). Spiked tar samples were prepared in dichloromethane from aliquots of the total tar sample by mixing with known amounts of authentic compounds.

Solid-phase extraction procedure

Each SPE amino column was conditioned prior to use by gravity feed elution of 0.5 ml of *n*-hexane. Aliquots of 1 ml of the tar extract were mixed with 100 μl of dichloromethane containing known amounts of 4-ethoxyphenol and 2-bromonaphthalene, serving as internal standards. From this mixture a 100-μl aliquot was withdrawn with a syringe and loaded onto the SPE column. Using gravity only, neutral compounds were eluted from the columns using four 100-μl aliquots of dichloromethane. Phenols were eluted with two 100-μl aliquots of dichloromethane–2-propanol (1:1, v/v) followed by three 100-μl aliquots of 2-propanol. To avoid cross-contamination and loss of sample components, the column tip was washed with small volumes of eluent following each fraction. Subsequently, the fractions were subjected to capillary GC after trimethylsilylation of the phenols (see *Derivatization*). Synthetic samples were similarly treated using the same sample volume. The adsorptive capacity of the sorbent was determined for phenol to be *ca.* 2% of the sorbent mass. The concentration of the tar mixture used in this study was *ca.* 26 mg/ml. This is equivalent to 2.6 mg applied to SPE columns. However, the best recoveries were obtained using a smaller sample size (less than 200 μg), as determined with synthetic samples.

Liquid–liquid extraction (LLE)

Aliquots of synthetic sample 3 (*ca.* 32 mg/ml) were mixed with internal standards and subjected to acid–base extraction in a glass-stoppered centrifugation tube. After extraction, the organic phases were dried over anhydrous sodium sulphate. The polar fraction was treated with BSTFA (see *Derivatization*) to convert the phenolic constituents into their trimethylsilyl derivatives prior to GC analysis.

Derivatization

Three different derivatization procedures were investigated for phenols: acetylation, methylation and silylation. For this study silylation was selected because of its simplicity and because the best GC resolution was obtained for isomeric compounds. The silylation was accomplished by reaction with an excess of BSTFA and dichloromethane as a cosolvent. The derivatization reaction was completed within 15–20 min at room temperature.

RESULTS AND DISCUSSION

The analytical procedure developed using capillary GC following SPE through amino phase columns was tested for selected phenols and aromatic hydrocarbons with

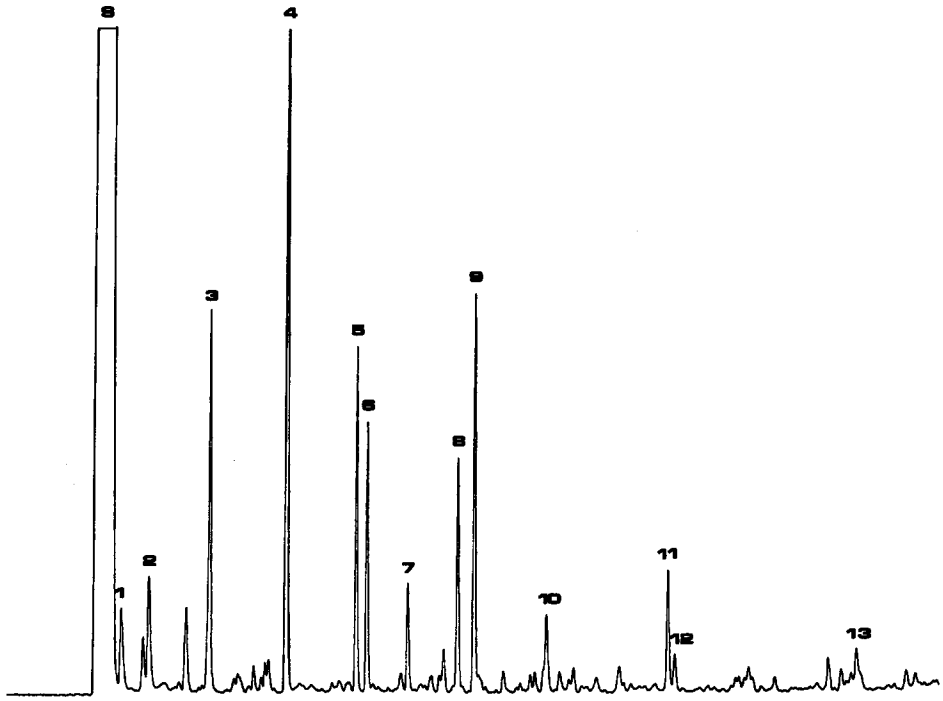

Fig. 1. Capillary GC of aromatic hydrocarbons. Peaks: 1 = toluene; 2 = *o*-xylene; 3 = indene; 4 = naphthalene; 5 = 2-methylnaphthalene; 6 = 1-methylnaphthalene; 7 = biphenyl; 8 = acenaphthylene; 9 = internal standard; 10 = fluorene; 11 = phenanthrene; 12 = anthracene; 13 = pyrene; S = solvent. Temperature programmed from 100 to 300°C at 8°C/min.

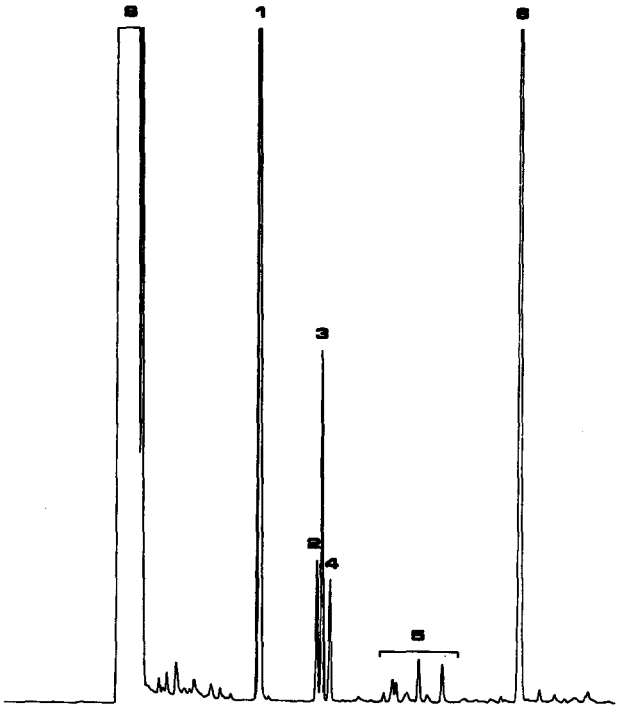

Fig. 2. Capillary GC of silylated phenolic compounds. Peaks: 1 = phenol; 2 = *o*-cresol; 3 = *m*-cresol; 4 = *p*-cresol; 5 = C_2-substituted phenols; 6 = internal standard; S = solvent. Temperature programmed from 100 to 220°C at 5°C/min.

TABLE I

REPRODUCIBILITY STUDY OF SPE AMINO COLUMNS FOR PRESEPARATION OF BIOMASS TAR

The number of SPE runs was 9. Eluted compounds were analysed by capillary GC in triplicate.

Compound	Mean value (μg)	Relative standard deviation (%)
Toluene	22.0	11.4
o-Xylene	36.6	9.4
Indene	131.7	0.6
Naphthalene	282.2	2.9
1-Methylnaphthalene	53.0	1.4
2-Methylnaphthalene	34.3	1.2
Biphenyl	13.5	1.7
Acenaphthylene	78.1	1.5
Fluorene	22.7	2.1
Phenanthrene	36.2	1.6
Anthracene	11.6	2.4
Pyrene	7.6	3.6
Phenol	156.4	1.0
o-Cresol	30.5	2.1
m-Cresol	60.3	1.0
p-Cresol	30.4	0.8

a high-temperature (800°C) biomass tar sample taken from a laboratory research pyrolysis unit. This type of tar contains only traces of amines and carboxylic acids which might interfere with the analysis of target compounds if present at higher concentrations. In order to obtain an adequate peak resolution for isomeric compounds, the phenols were converted into their trimethylsilyl analogues prior to GC analysis. Typical gas chromatograms of neutral and polar SPE fractions are shown in Figs. 1 and 2, respectively.

The reproducibility was evaluated by nine replicate analyses of a tar sample. Each SPE fraction was analysed in triplicate by GC. The average results given in Table I demonstrate that good precision was obtained for all compounds except toluene (*ca.* 11%) and *o*-xylene (*ca.* 9%).

The accuracy of the method was established by analysing alquots of synthetic samples containing seven phenols and eleven aromatic hydrocarbons at two concentration levels (1.9 and 9.7 mg/ml). Further recovery data were obtained from the analysis of a tar sample spiked with selected authentic compounds. The results from SPE were compared with those obtained by LLE traditionally used in much

TABLE II

COMPARISON OF THE RESULTS OF SPE AND LLE OF SYNTHETIC SAMPLES AND A SPIKED TAR SAMPLE

Eluted compounds were analysed by capillary GC in triplicate. Synthetic sample 1: concentration = 1.909 mg/ml, sample size ≈ 191 μg. Synthetic sample 2: concentration = 9.672 mg/ml, sample size ≈ 967 μg. Synthetic sample 3: concentration = 32.060 mg/ml, sample size ≈ 3.2 mg. Spiked tar sample: concentration = 3.184 mg/ml, sample size ≈ 318 μg.

Compound	Recovery (%)			
	SPE			LLE: Synthetic sample 3[d]
	Synthetic sample 1[a]	Synthetic sample 2[b]	Spiked tar sample[c]	
Phenol	94	86	–	68
o-Cresol	100	82	82	96
m-Cresol	101	85	–	94
p-Cresol	105	85	92	92
o-Ethylphenol	101	75	–	94
2,5-Xylenol	96	77	–	89
3,4-Xylenol	106	87	87	94
Toluene	108	92	–	86
o-Xylene	102	92	–	85
Naphthalene	94	75	–	80
2-Methylnaphthalene	88	85	98	86
1-Methylnaphthalene	92	78	93	86
Biphenyl	102	85	98	88
Acenaphthylene	93	65	–	85
Fluorene	76	85	–	88
Phenanthrene	77	105	–	109
Anthracene	79	86	–	92
Pyrene	85	116	–	100

[a,c] Average of two analyses.
[b,d] Average of three analyses.

quantitative work for the separation of polar and non-polar compounds. All recovery data are summarized in Table II.

From the measurements reported for sample 2 (high-concentration synthetic sample) an overall efficiency of 86% was obtained. Individual values ranged from 75 to 87% for phenols and from 65 to 116% for neutral compounds. The effects of using a smaller sample size (sample 1) are also illustrated in Table II. In this instance the overall recovery was 94%, an improvement of 8% over the high-concentration sample. Individual values were in the range 94–106% for phenols and 76–108% for neutral species. The results from the study performed with a spiked tar sample also showed good recovery (overall *ca.* 92%). In comparison, the overall efficiency for LLE (by means of three successive partitions) was 90%, with individual values in the range 68–96% for phenols and 80–109% for aromatic hydrocarbons. As is evident from the comparative results given in Table II, the overall recovery (94%) obtained by SPE (sample 1) agrees favourably with the results (90%) from LLE. Furthermore, the SPE recoveries were almost quantitative ($\geqslant 92\%$) for thirteen of the eighteen analytes compared with eight compounds for LLE. These data also show that the efficiency of the SPE procedure increased with a decrease in sample size, although this finding is most pronounced for phenols. Efficient separations using SPE are thus demonstrated. The tar used in this work also contains heavy tar components of low volatility such as pre-asphaltenes (constituting *ca.* 20 wt.-%), which are not analysable by GC but may interfere with the analysis, resulting in non-reproducibility of the results. To remove these components, solvent precipitation using *n*-alkane solvents is traditionally used. However, most of these components are effectively retained by the SPE amino-sorbent used in this work, and are thus separated from the target compounds. Owing to the highly polar nature of the amino-sorbent employed, phenols are expected to be very strongly retained. This is also true of the target compounds. However, we found that 2,6-di-*tert.*-butyl-4-methylphenol, reported to be present in pyrolytic biomass oil [10], and 3,5-di-*tert.*-butylphenol co-eluted with the aromatic hydrocarbons. This different behaviour may be due to the weakening of acidity caused by the inductive effects of the electron-repelling *tert.*-butyl groups in combination with steric hindrance which prevented effective interaction with the adsorbent. However, no *tert.*-butyl-substituted phenolic compounds were detected in the tar sample used in this study.

Summarizing the results, it may be concluded that the use of SPE for the analysis of high-temperature biomass tar circumvents the problems associated wtih LLE, thus providing a better alternative to this traditional preseparation technique.

CONCLUSIONS

An efficient method was developed for determination of selected phenols, alkylated aromatics and polycyclic aromatic hydrocarbons in biomass tar using SPE amino columns in combination with capillary column GC. The method was found to be rapid, highly reproducible and accurate, and is suggested as a better alternative to LLE, traditionally employed for chemical class separation prior to GC analysis.

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