

Note

Quantitative structure-type analysis of hetero compounds–hydrocarbon mixtures

Analysis of S-heterocyclics and ketones from brown coal tars

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The working-up properties of brown coal tars and the quality of the products from it, such as paraffins, components for gasoline and diesel oils, lubricating oil components and electrode coke, are determined by the chemical composition of the tars. The hetero compounds present are converted during thermal pyrolysis or hydrogenation processes. The chemical conversions in the working-up processes are described only by the qualitative and quantitative structure-type analysis of the tar, charge substances and reaction products.

In previous papers^{1,2} we reported on the development of an on-line method for the semi-preparative structure-type analysis of hetero compounds–hydrocarbon mixtures, such as tars and coal hydrogenation products. The application of this method to the determination of compounds that are typical of the nature of the coal conversion process^{3,4} and to the determination of the chemical conversion of coals, tars and lubricating oil components in technical processes^{3,5–7} was described.

S-Heterocyclics present in brown coal hydrogenation products are eluted by chromatography on normal phases according to their chemical properties with aromatics with the same number of π -electrons³. Thus, benzothiophene and its alkyl-substituted homologues are eluted together with dicyclic aromatics. The S-heterocyclics in this fraction were detected by capillary gas chromatography–mass spectrometry (GC–MS).

Gundermann *et al.*⁸ and Nishioka *et al.*⁹ separated S-heterocyclics from aromatic fractions obtained by the liquid chromatography of coal conversion products on an aluminium oxide–silica gel column forming complexes on a palladium chloride–silica gel phase (“fixed-phase extraction”). The palladium chloride–S-heterocyclic complexes were eluted from this phase with dichloromethane and decomposed with ammonia. The S-heterocyclics were identified by GC–MS.

The problem in this work was to separate the group of hetero compounds with similar elution properties to aromatic hydrocarbons by a fixed-phase extraction step in the on-line analysis method, and to identify the individual compounds by capillary GC.

EXPERIMENTAL

The separation scheme according to Zobel and co-workers^{2,4} for on-line structure-type analysis was modified by inserting a complex formation step on a palladium chloride-silica gel phase column (100 mm × 8 mm I.D.) between the first precolumn and the silica-i-60-NH₂ phase column as a second precolumn. The modified separation scheme is shown in Fig. 1 and the resulting scheme for the semi-preparative high-performance liquid chromatographic (HPLC) apparatus in Fig. 2.

The palladium chloride-silica gel phase was prepared according to Nishioka *et al.*⁹. The eluents and the phase materials for the hydrocarbons and for the back-flushing of the hetero compounds are given in Fig. 1. The hetero compounds were separated into acidic (AHC), basic (BHC) and neutral hetero compounds (NHC) by application of an anion exchanger (Amberlite IRA-904) and a cation exchanger (Amberlyst A-15).

The palladium chloride-hetero compounds complexes were eluted from pre-column II with hexane-dichloromethane (90:10) and were decomposed on a small

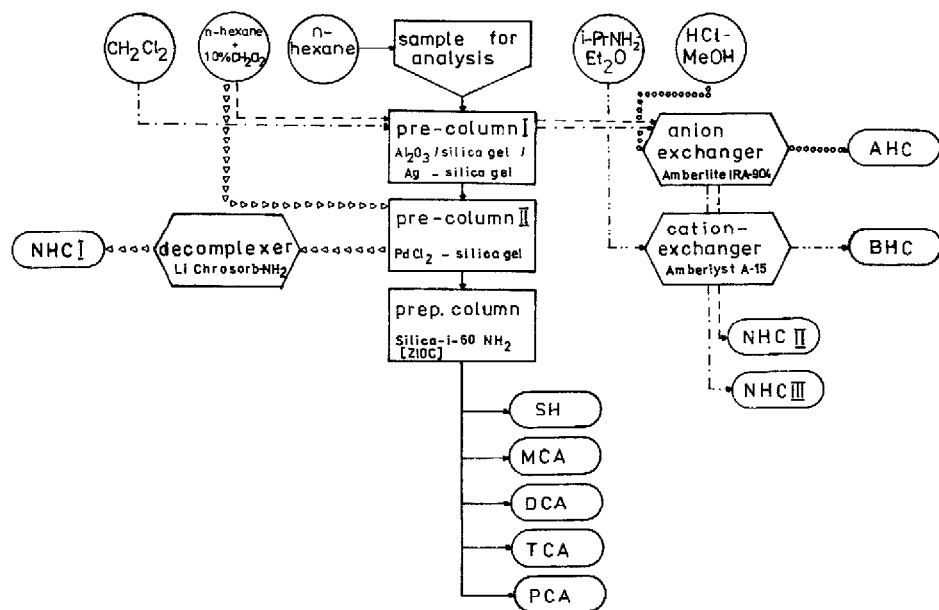


Fig. 1. Scheme of the structure-type separation by semi-preparative HPLC. SH = saturated hydrocarbons; MCA = monocyclic aromatics; DCA = dicyclic aromatics; TCA = tricyclic aromatics; PCA = polycyclic aromatics; AHC = acidic hetero compounds; BHC = basic hetero compounds; NHC = neutral hetero compounds. Et = Ethyl; Me = methyl; i-Pr = isopropyl.

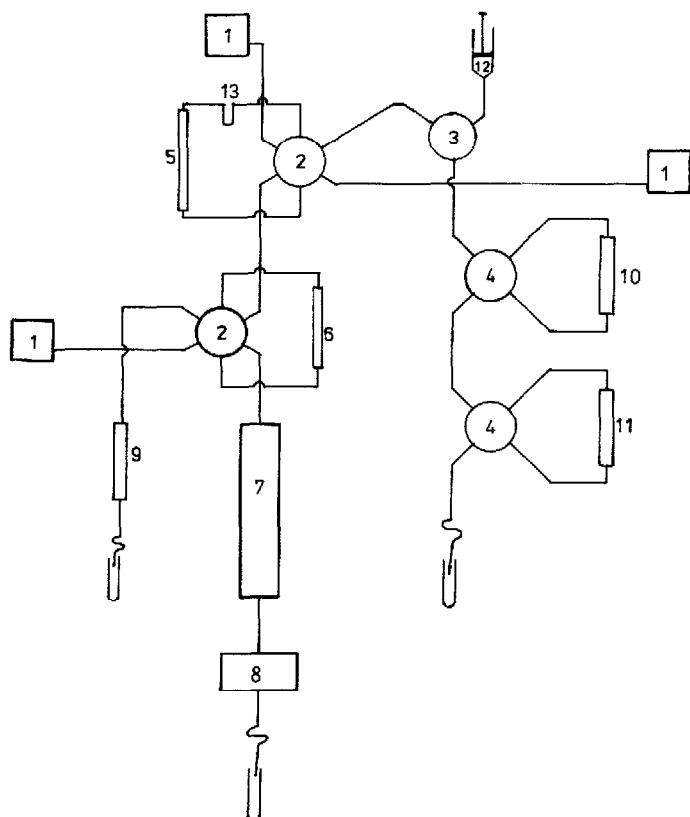


Fig. 2. Apparatus for on-line semi-preparative structure-type analysis. 1 = Pump; 2 = 6-port valve; 3 = 3-port valve; 4 = 4-port valve; 5 = precolumn I; 6 = precolumn II; 7 = separation column; 8 = differential refractometer; 9 = decomplexer column; 10 = anion-exchange column; 11 = cation-exchange column; 12 = injection syringe; 13 = sample loop.

decomplexing column filled with LiChroprep-NH₂ (100 mm × 8 mm I.D.). The eluate was evaporated in a stream of nitrogen and the amount of the hetero compounds was determined gravimetrically (NHC-I fraction).

The analytical rechromatography by HPLC, the quantitative interpretation of the structure-type analysis and the GC-MS conditions were described in a previous paper⁴. The individual compounds in the NHC-I fraction were identified by capillary GC with flame ionization detection (FID), flame photometric detection (FPD) and coupling with a mass spectrometer.

The following conditions for capillary GC were adopted: apparatus, Sichromat 1 with FPD and FID (Siemens); column, 15 m × 0.3 mm I.D. fused silica with DB-5; pressure, 0.18 MPa (nitrogen); injector temperature, 623 K; and temperature programme of the column oven, 313–573 K at 3 K/min.

TABLE I

STRUCTURE-TYPE COMPOSITION OF THE TAR OIL (b.p. > 598 K) FROM THE DISTILLATION OF A BROWN COAL TAR

Structure type ^a	Concentration (%)	Qualitative composition
SH	34.2	Paraffins > olefins > naphthenes
MCA	9.5	Alkyl benzenes tetralenes, indanes
DCA	7.1	Naphthalenes, acenaphthenes > diphenyls, fluorenes
TCA	7.3	Phenanthrenes > anthracenes
PCA	2.7	Pyrenes, chrysenes
AHC	7.5	Phenols, indanols
BHC	1.5	
NHC I	5.8	Aliphatic ketones, benzothiophenes, dibenzothiophenes
NHC II	18.3	
NHC III	5.8	

^a See Fig. 1.

RESULTS

The results obtained are demonstrated by the analysis of a tar oil (b.p. > 598 K) from the distillation of a low-temperature brown coal tar. The structure-type composition and quality the principal groups obtained are given in Table I. The semi-preparative HPLC results are presented in Fig. 3.

By complex formation on the palladium chloride-silica gel phase the NHC-I fraction was separated, constituting 5.8% of the tar oil. Homologous series of peaks are shown in the capillary gas chromatogram (Fig. 4). These homologous series were identified by GC-MS as aliphatic ketones with carbonyl groups at the 2-, 3-, 4- and 5-positions in the alkyl chain. Phenanthraquinone is present in trace amounts. The alkanones are products of the thermal destruction of brown coal waxes^{10,11}.

Dibenzothiophene and its C₁-C₃₊-alkyl-substituted homologues were detected and identified by GC-MS with method of the selective trace. With FPD a capillary gas chromatogram was obtained in which only the peaks of the S-heterocyclics were present (Fig. 5), from which their amount was determined.

The composition of the NHC-I fraction is given in Table II. The principal components are the alkanones, constituting 4.9% of the tar oil. Dibenzothiophene and its alkyl-substituted homologues constituted 0.85% of the tar oil. These represent 93% of the tar oil S-hetero compounds.

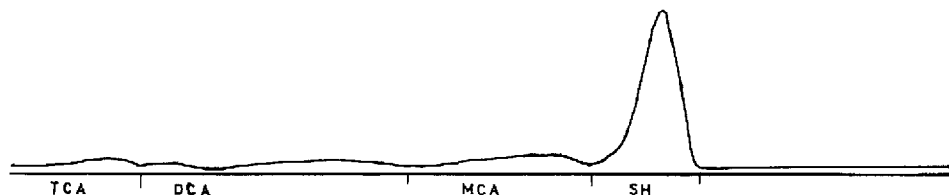


Fig. 3. Semi-preparative HPLC trace for a tar oil (b.p. > 598 K) from the distillation of a brown coal tar.

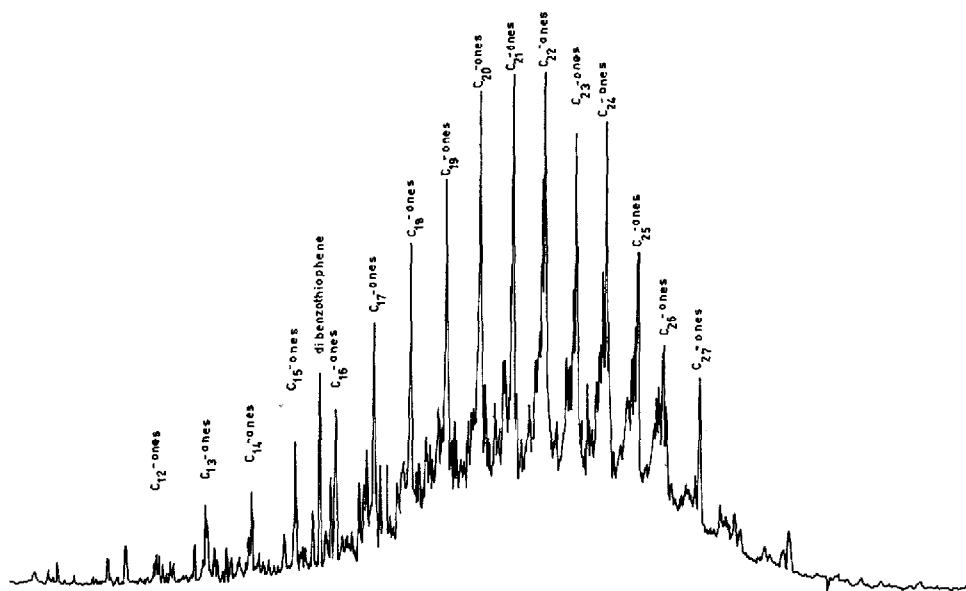


Fig. 4. Capillary gas chromatogram of the NHC I fraction with FID.

C_1 -di benzo-
thiophenes

 C_3 -dibenzothiophenes

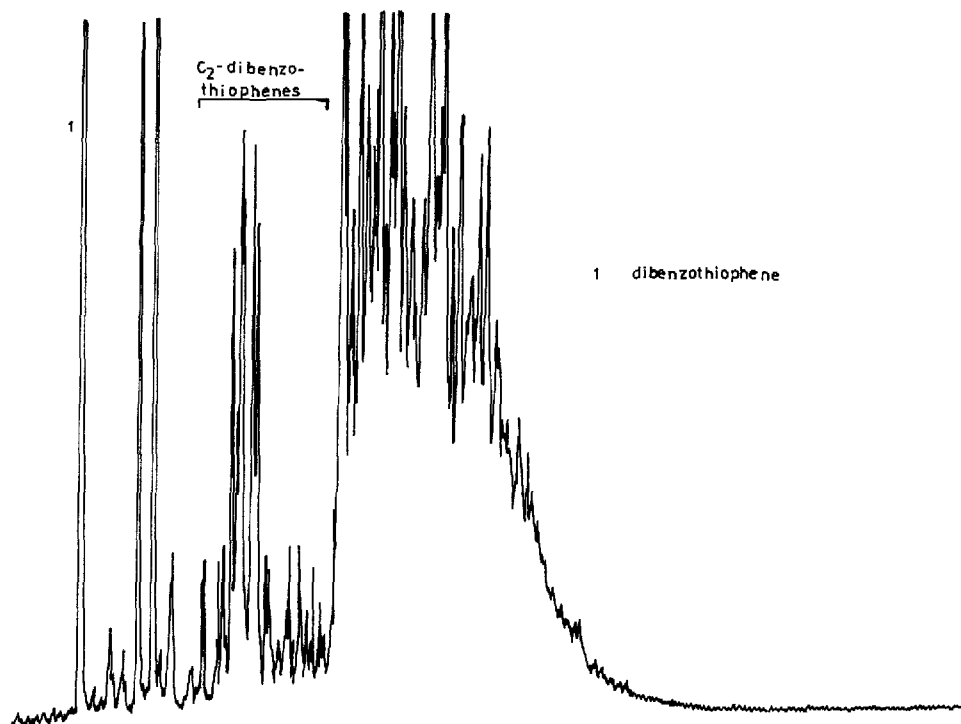


Fig. 5. Capillary gas chromatogram of the NHC I fraction with FPD.

TABLE II
COMPOSITION OF THE NHC I FRACTION BY CAPILLARY GC

<i>Compounds</i>	<i>Proportion of the fraction (%)</i>	<i>Proportion of the tar oil (%)</i>
<i>Alkanones:</i>	85.3	4.9
Alkan-2-ones	41.8	2.4
Alkan-3-ones	43.5	2.5
Alkan-4-ones		
Alkan-5-ones		
<i>Dibenzothiophes:</i>	14.7	0.85
Dibenzothiophene	0.8	0.05
C ₁ -Dibenzothiophenes	1.8	0.1
C ₂ -Dibenzothiophenes	2.6	0.15
C ₃ -Dibenzothiophenes	9.5	0.55

CONCLUSIONS

S-Heterocyclics and aliphatic ketones are separable as a group from brown coal tars by complex formation with palladium chloride. A requirement is that the hetero compounds with acidic and basic properties and with neutral OH groups and neutral N-bonding forms are separated previously.

The selectivity of palladium chloride complex formation, as described by Gundermann *et al.*⁸ and Nishioka *et al.*⁹, is not limited to the S-heterocyclics.

The group separation accomplished effects a clear improvement of the identification of S-heterocyclics and alkanones in tars.

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