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Use of Capillary Column Gas Chromatography to Evaluate the Quality of Coal Tar Pitches

R. F. Arrendale[a]; L. B. Rogers[b]
[a] TOBACCO AND HEALTH LABORATORY SCIENCE AND EDUCATION ADMINISTRATION/AGRICULTURAL RESEARCH U.S. DEPARTMENT OF AGRICULTURE ATHENS, GEORGIA [b] DEPARTMENT OF CHEMISTRY, UNIVERSITY OF GEORGIA ATHENS, GEORGIA

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NOTE

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R. F. ARRENDALE

TOBACCO AND HEALTH LABORATORY
SCIENCE AND EDUCATION ADMINISTRATION/AGRICULTURAL RESEARCH
U.S. DEPARTMENT OF AGRICULTURE
ATHENS, GEORGIA 30613

L. B. ROGERS

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF GEORGIA
ATHENS, GEORGIA 30602

Abstract

A combination of a room-temperature extraction of coal tar pitch, silicic acid adsorption chromatography to isolate the polynuclear aromatic hydrocarbon fraction, and capillary gas chromatography has been shown to provide an unambiguous basis for estimating the quality of thermic electrodes produced from that pitch. When portions of the extracts from three grades of pitches were analyzed quantitatively for several compounds in the volatility range from phenathrene to benzo[*a*]pyrene, the amounts of each of six species in the less volatile range changed inversely with pitch quality.

INTRODUCTION

Coal tar pitches are obtained as residues from distillations. The pitches, which are known to be high in aromatic content, find many uses in industry, especially in the production of thermic electrodes (*1*). In an earlier paper we reported the successful correlation of pyrolysis–gas chromatography with the quality of thermic electrodes produced when using those pitches (*2*). In addition, several peaks in the pyrograms were tentatively identified by showing that their retention times agreed with those for known polynuclear aromatic hydrocarbons (PAH). However, because those pyrograms were obtained using packed columns, a peak might have represented two or more components. Hence it was desirable to repeat parts of that study using higher chromatographic resolution. In addition, it was desirable to determine whether the compounds in question were present originally or were produced by the pyrolysis process. For that reason a room-temperature liquid extraction was used to remove PAH from a coal tar and, after clean-up by a silica adsorption column, portions of the extract were subjected to capillary gas chromatography. Again, as in the original study, standard samples of several pure PAH were used to calibrate the retention times and identify species. In addition, the area responses of the capillary system were also calibrated for several PAH that covered a relatively wide range of volatilities as indicated by their retention times.

EXPERIMENTAL

Gas Chromatography (GC)

The PAH standards used for determinations of GC response data were purified by chromatography on a short silicic acid (SA) column with benzene/petroleum ether (PE) (1:3, v/v) and were then recrystallized from methanol.

Capillary column GC response data and GC separations of the PAH from the coal tar pitches were obtained using a Hewlett-Packard Model 5840A gas chromatograph that was equipped with a 18835A capillary inlet system and a 30 m × 0.25 mm i.d. WCOT glass capillary column coated with SE-54 by a modified version of the Grob $BaCO_3$ procedure (*3*, *4*) temperature program for split-injection mode: 60–250°C at 4°/min, 40 cm/s He linear velocity at 60°C, 80:1 split ratio, 290°C injector temperature and 300°C flame ionization detector (FID) temperature. Make-up gas (He) was added to the FID just before the capillary column exit. (Reference to a company or product name does not imply approval or recommendation by the USDA.)

The GC response characteristics using the WCOT column were determined by analysis of a standard PAH mixture containing known amounts of PAH covering the volatility range from naphthalene to BaP. Standard mixtures were injected manually using a 10-μL syringe in the following manner: 2 μL of isooctane was drawn into the syringe separated by a μL of air; another μL of air was drawn into the syringe followed by 1 μL of standard PAH mixture; the standard mixture and wash solvent (isooctane) were injected and the syringe needle was allowed to remain in the injection port for 5 s after injection. The PAH isolated from the coal tar pitches were injected in the same manner. In all cases, the reproducibility of each response factor was good, i.e., 6% or less.

Injection of standard PAH mixtures without a plug of wash solvent failed to transfer the compounds quantitatively from the syringe needle and caused erratic and irreproducible results. The cause of this behavior was probably fractional distillation of the PAH from the syringe needle after injection but before the needle was removed from the injection port.

Isolation Procedure for Polynuclear Aromatic Hydrocarbons

Approximately 0.5 g of coal tar pitch, which had been ground to 100 mesh, was transferred to a 500-mL flat-bottom long-neck flask and 100:50:50 mL of benzene/methanol/ether was added. All solvents (Burdick and Jackson Laboratories glass-distilled type) were redistilled through a 200-cm Vigreaux-type distilling column. The flask was placed in an ultrasonic bath and the pitch was extracted for 1 h at room temperature. The entire contents of the flask were quantitatively transferred to a 1000-mL round-bottom flask with 100 mL of benzene and 100 mL of methanol. Forty grams of silicic acid (SA, 100 mesh, Mallinckrodt, washed with methanol and activated in a forced air oven at 150°C for 18 h) and 200 mL

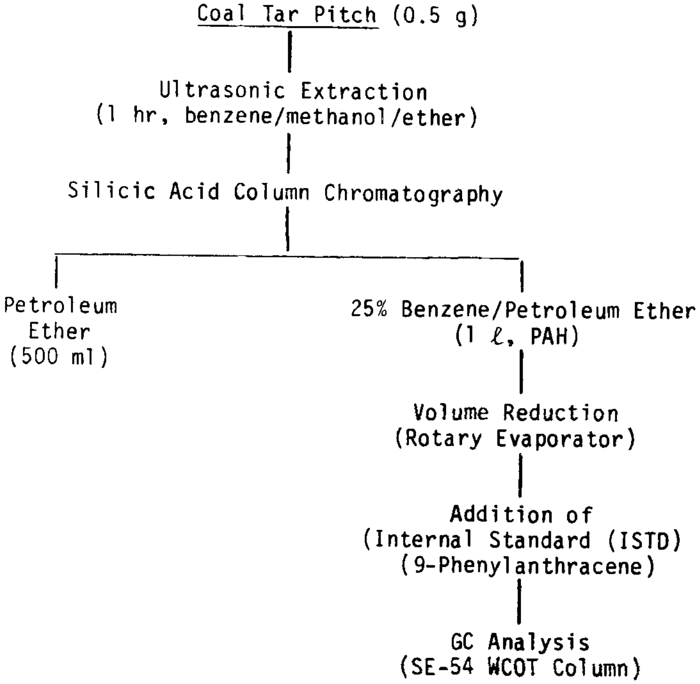

FIG. 1. Separation of polynuclear aromatic hydrocarbons (PAH) from coal tar pitch.

of isooctane were added to the flask. The flask was then placed on a Buchler flash (rotary) evaporator, and the benzene, ether, methanol, and a small portion of the isooctane were removed. The remaining mixture of SA, sample, and isooctane was slurried with 200 mL of petroleum ether (PE) and quantitatively transferred to the top of a 3.4 cm i.d. × 50 cm glass column equipped with a 35/25 socket joint for connection and operated at a pressure of 8–10 psi of nitrogen. The column was packed with 100 g of SA as a slurry in PE. The column was first eluted with 500 mL of PE to yield a paraffinic hydrocarbon-containing fraction and then eluted with 1 L of 25% benzene in PE (v/v) to yield the PAH material. The solvent volume was reduced to less than 5 mL with a Buchler flash evaporator, and the remainder was quantitatively transferred to a 5-mL volumetric flask and its volume was adjusted to 5 mL with isooctane. Fifty microliters of the PAH fraction was transferred to a tapered test tube, and 200 to 400 μL of an internal standard mixture (9-phenylanthracene, 1.9 μg/μL) was added.

Our scheme for the isolation of PAH from the coal tar pitches (Fig. 1) is based in part on a scheme developed by Severson et al. (*5*). The isolation scheme was verified for quantitative recovery of PAH by adding ^{14}C-BaP to the flask containing a coal tar pitch just before extraction. The benzene–petroleum ether fraction from the SA column yielded 99% of the initial ^{14}C-BaP activity.

RESULTS

In order to quantitate the PAH in the coal tar pitches, a suitable internal standard (ISTD) had to be found. GC analysis of each PAH fraction indicated an open retention window for 9-phenylanthracene; therefore, it was chosen as the ISTD. Figure 2 shows a typical chromatogram of the PAH fraction from a coal tar pitch, in this case, pitch ϕ (CTP-ϕ) plus the ISTD (9-phenylanthracene). Then, response data (weight/area) were determined for each compound in standard mixture of PAH based upon unit response for 9-phenylanthracene (Table 1). Note that, although the values generally rose as the retention times increased, all were within ±15% of unity. Furthermore, the relative standard deviation for results for each species was found to be less than 6%.

Using those response factors, quantitative data for PAH from coal tar pitch ϕ were obtained using the split injection mode (Table 2). Again, note the good reproducibilities even for the complex, high-boiling components where nonlinearity in the response is known to occur. As expected, the highest relative percent error (RPE) occurred for the minor components.

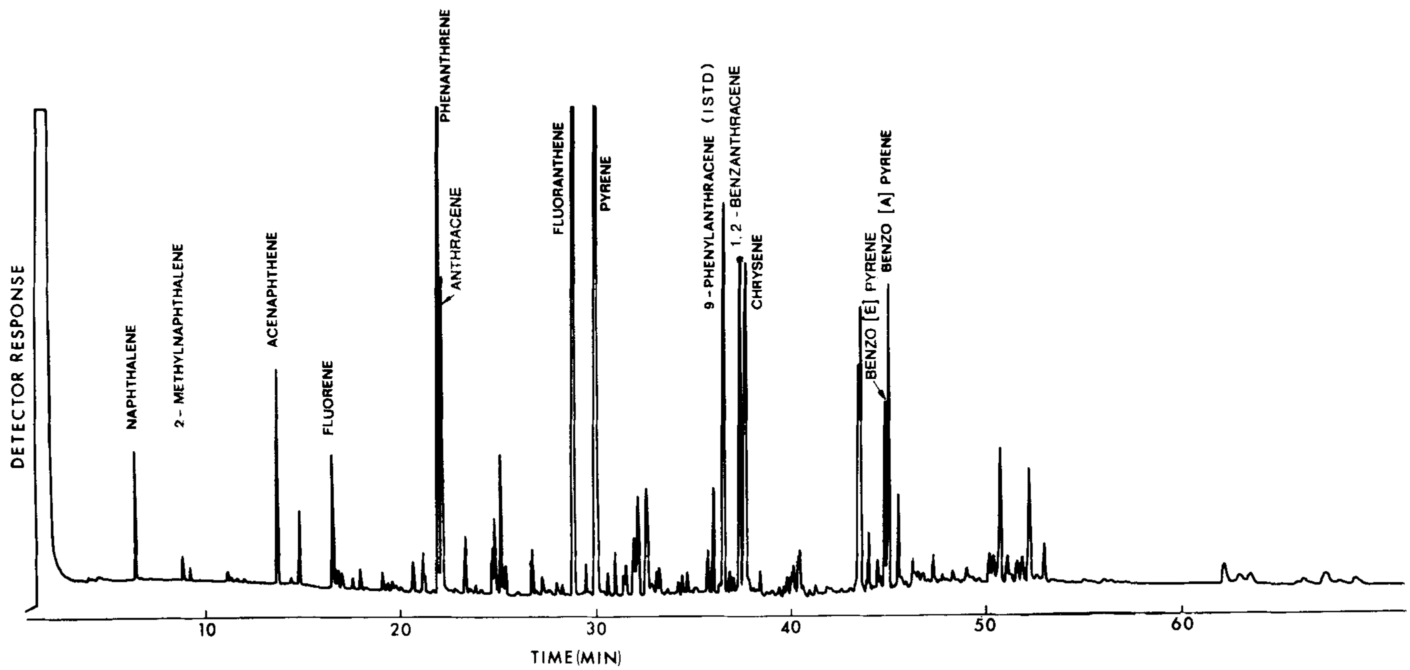

FIG. 2. Polynuclear aromatic hydrocarbons (PAH) fraction derived from a coal tar pitch. Chromatogram obtained using an SE-54 WCOT column. Conditions: 30 m × 0.25 mm i.d.; temperature programmed from 80 to 250°C at 5°/min; 35 cm/s helium flow, split injection mode; flame ionization detector.

TABLE 1

Gas Chromatographic Response Factors (RF of 9-Phenylanthracene = 1) of a Polynuclear Aromatic Hydrocarbon Standard Mixture on an SE-54 WCOT Column with the Split Injection Mode

Compound	RF[a]
Naphthalene	0.86
2-Methylnaphthalene	0.86
Acenaphthene	0.89
Fluorene	0.86
Phenanthrene	0.85
Fluoranthene	0.87
Pyrene	0.87
Benzo[*ghi*]fluoranthene	0.94
9-Phenylanthracene	1.00
Chrysene	1.00
Benzo[*a*]pyrene	1.10

[a] Average of three analyses.

TABLE 2

Quantitation of Polynuclear Aromatic Hydrocarbons in Coal Tar Pitch ϕ Separated on an SE-54 WCOT Column with the Split Injection Mode (Internal Standard = 9-Phenylanthracene)

Compound	mg/g[a]	SD[b]	RPE[c]
Naphthalene	2.2	±0.1	6
2-Methylnaphthalene	0.2	±0.05	12
Acenaphthene	5.7	±0.3	5
Fluorene	4.0	±0.3	8
Phenanthrene	40.3	±1.7	5
Fluoranthene	38.8	±1.1	3
Pyrene	34.9	±1.4	4
Benzo[*ghi*]fluoranthene	3.4	±0.1	3
Chrysene	17.0	±0.4	2
Benzo[*a*]pyrene	13.1	±0.6	5

[a] Average of three analyses.
[b] SD = standard deviation.
[c] RPE = relative percent error.

The next step was to measure the levels of PAH from three different qualities of coal tar pitches (ϕ, 6A, and 2A) using the SE-54 WCOT column in the split mode of injection. In the production of graphite products, 6A is considered to be a very good pitch, 2A a fair pitch, and ϕ a poor pitch. As shown in Table 3, no correlation can been seen between pitch quality and the amount of a low-boiling PAH (naphthalene to fluorene). However, there was a very good inverse correlation between pitch quality

TABLE 3

Quantitation of Polynuclear Aromatic Hydrocarbons in Three Typical Coal Tar Pitches by Gas Chromatography on an SE-54 WCOT Column with the Split Injection Mode

Compound	Pitch (mg/g)		
	6A	2A	ϕ
Naphthalene	6.2	0.1	2.2
2-Methylnaphthalene	0.8	2.7	0.4
Acenaphthene	2.0	1.2	5.7
Fluorene	1.7	0.8	4.0
Phenanthrene	7.5	13.8	40.3
Fluoranthene	5.2	17.3	38.8
Pyrene	4.5	15.1	34.9
Benzo[*ghi*]fluoranthene	0.4	1.8	3.4
Chrysene	2.6	8.2	17.0
Benzo[*a*]pyrene	4.5	6.6	13.2

and the amounts of medium and high boiling PAH (phenanthrene to BaP). Hence, it appears that the use of a room-temperature liquid extraction procedure followed by a capillary gas chromatographic analysis for quantitation of PAH should provide an unambiguous method for estimating the quality of a coal tar pitch that is to be used to produce thermic electrodes.

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