Journal of Chromatography, 241 (1982) 33–39
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 14,704

DETERMINATION OF CONTAMINANTS IN ANTHRACENE BY GAS CHROMATOGRAPHY USING A LIQUID CRYSTALLINE STATIONARY PHASE

KRYSTYNA KUBICA
Institute for the Chemical Processing of Coal, 41-803 Zabrze 3 (Poland)
and
ZYGFRYD WITKIEWICZ*
Institute of Chemistry, Military Technical Academy, 01-489 Warsaw 49 (Poland)

SUMMARY

The separation of contaminants in anthracene and the determination of phenanthrene, carbazole and fluoranthene with triphenylmethane as an internal standard are described. These compounds and others that occur in the mixture in various amounts can be determined with the application of a new high-temperature liquid crystalline stationary phase. The precision of the method has been calculated.

INTRODUCTION

Anthracene and its derivatives are intermediates in the synthesis of dyestuffs, scintillators and other substances, and the testing of the purity of anthracene and the determination of the contaminants (mainly phenanthrene and carbazole are therefore important commercial problems. The determination of these contaminants has been performed by various methods, which can be classified into several groups in which use is made of the chemical, optical and electrochemical properties of anthracene as well as of the differences in the solubilities and adsorptions of anthracene and its contaminants.

The principal chemical method of determining anthracene is its oxidation by means of chromium trioxide to anthraquinone and subsequent gravimetric determination of the latter[1–3]. The results obtained in this method depend on many parameters, *e.g.*, the concentration of the oxidizing agent and its excess, time of oxidation and the volumes of the reaction mixture and solutions used for washing. As a result, the method suffers from considerable errors. Another chemical method of determining anthracene consists in obtaining adducts with maleic anhydride in xylene[4] or chlorobenzene[5,6].

UV and IR spectrometry have also been used for determining anthracene. By UV spectrometry anthracene, phenanthrene and carbazole were determined in their mixtures[7–9]. Lipatowa and Biednow[10], Srap and Utynon[11] and Kekin and Kornilowa[12] used IR spectrometry for the same purpose. Spectrophotometric methods are, how-

0021-9673/82/0000–0000/$02.75

ever, of insufficient accuracy on account of the limited resolving power of spectrophotometers[13].

Anthracene, phenanthrene, carbazole and other high-boiling aromatic compounds have also been determined by polarography[14,15] and by paper[16], thin-layer[17] and partition gas–liquid chromatography[18]. Kipot *et al.*[19] recommended the use of mass spectrometry for determining high concentrations of anthracene.

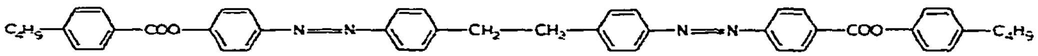
In recent years gas chromatography has been the most widely used method for the determination of anthracene, phenanthrene and carbazole and of many other organic compounds (including polynuclear aromatic hydrocarbons), most commonly with OV-17[20], Dexil 300[21], graphitized carbon black[22–24] and SE-52 (in a capillary column)[25] as stationary phases. The greatest difficulty, encountered with most stationary phases, is the separation of phenanthrene from anthracene. A good separation of these two substances, like that of many other isomers, can be achieved on liquid crystalline stationary phases[26–31]. In this work an attempt was made to apply new liquid crystalline stationary phases for the determination of phenanthrene and carbazole in chemically pure and commercial anthracene.

EXPERIMENTAL

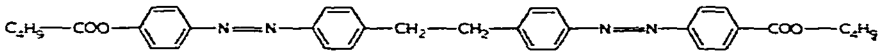
Stationary phases

Two liquid crystalline stationary phases, obtained from the Military Technical Academy, Warsaw, with the formulae

(I)



(II)



were used. The procedure of obtaining I will be described elsewhere, and II was obtained by a method published recently[32]. Stationary phase I melts at 195°C and is converted into the smectic phase; the transition to the nematic phase takes place at 217°C and to the isotropic liquid at 350°C. The corresponding temperatures for II are 165, 184 and 303°C.

Columns

The liquid crystals were deposited on Chromosorb W AW DMCS (60–80 mesh) from chloroform solution. The actual amount of stationary phase on the support was determined by removing the former from the support at 600°C. The columns used were made of stainless steel, 2 m long and 2.2 mm I.D. The characteristics of the columns are given in Table I.

Apparatus and procedure

The tests were carried out using a Perkin-Elmer F-11 gas chromatograph with a flame-ionization detector. The temperature of the injector was 300°C. Argon was used as the carrier gas, whose optimal flow-rate of 20 cm^3/min was determined from measurement of the HETP.

The first stage of work consisted in checking whether both stationary phases

TABLE I

CHARACTERISTICS OF THE COLUMNS

Column	*Stationary phase*	*Actual concentration of stationary phase on support (%)*	*Amount of filling (g)*
1	I	2.52	2.05
2	II	4.85	1.95

are suitable for use in the quantitative analysis of anthracene–phenanthrene–carbazole mixtures. It was found that good separations of the mixtures are obtained with satisfactory analysis times at 200 and 195°C for I and II, respectively.

This corresponds to the smectic structure of the mesophase for I and the nematic structure for II. The retention times for the same compounds are shorter on I. An increase in the concentration of I on the support to about 5% has no major effect on the improvement of the separation, whereas a decrease in the concentration of II to about 2.5% has a negative effect.

RESULTS AND DISCUSSION

The retention times of the substances present in anthracene relative to triphenylmethane (internal standard) are given in Table II. The results show that triphenylmethane can be used as the internal standard only for column 1, because in column 2 a poor separation from phenanthrene is achieved in the absence of diphenyl sulphide (Fig. 1). The components of mixtures were identified by comparison with known compounds. For II dihydroanthracene could be used as internal standard, but it was

TABLE II

RELATIVE RETENTION TIMES

Compound	*Column*	
	1	*2*
Naphthalene	0.28	0.15
Biphenyl	0.33	0.20
α- and β-methylnaphthalenes	0.35	0.22
Dimethylnaphthalenes	0.38	0.24
Acenaphthene	0.48	0.30
Diphenyl oxide	0.61	0.37
Fluorene	0.76	0.47
Triphenylmethane*	1.00	1.00
Diphenyl sulphide	1.46	1.00
Phenanthrene	1.69	1.07
Anthracene	2.08	1.30
Acridine	2.90	1.57
Methylanthracene	—	1.81
Carbazole	3.35	2.07
Fluoranthene	5.17	2.47
Pyrene	5.92	3.28

* Internal standard.

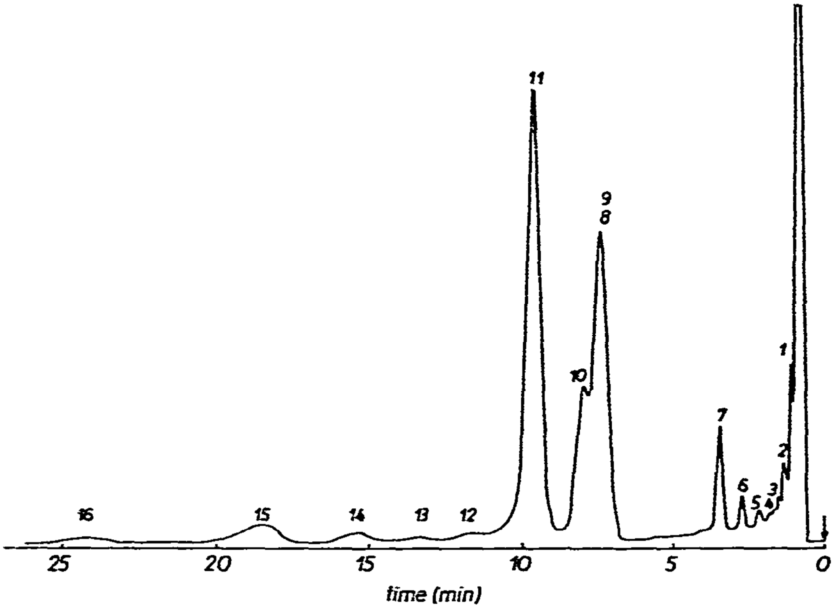


Fig. 1. Chromatogram of commercial anthracene with added of triphenylmethane. Stationary phase II; column 2; column temperature, 195°C; carrier gas, argon; flow-rate, 20 cm^3/min. Peaks: 1 = naphthalene; 2 = biphenyl; 3 = α- and β-methylnaphthalenes; 4 = dimethylnaphthalene; 5 = acenaphthene; 6 = diphenyl oxide; 7 = fluorene; 8 = triphenylmethane; 9 = diphenyl sulphide; 10 = phenanthrene; 11 = anthracene; 12 = methylanthracene; 13 = acridine; 14 = carbazole; 15 = fluoranthene; 16 = pyrene.

found that it contained contaminants such as phenanthrene, anthracene and carbazole, which were not detected in triphenylmethane. The determination of anthracene contaminants was therefore performed on I.

Preliminary tests of the determination of contaminants in anthracene were made using standard mixtures containing various amounts of phenanthrene, anthracene and carbazole. The possibilities of separating the components of these mixtures were tested and the accuracy of the determination was determined. The compositions of the standard mixtures are given in Table III. The standard mixtures, like the samples tested, were dissolved in benzene–toluene–xylene (1:1:1.5). Chromatograms of the standard mixture and anthracene are presented in Figs. 2 and 3.

The proposed method was used for determining phenanthrene, anthracene and carbazole in commercial anthracene (known as 40% product) and chemically pure

TABLE III

COMPOSITIONS OF STANDARD MIXTURES

Composition	*Concentration in mixtures (%)*		
	1	*2*	*3*
Phenanthrene	4.53	0.35	23.10
Anthracene	89.54	95.01	26.55
Carbazole	5.93	4.64	50.35

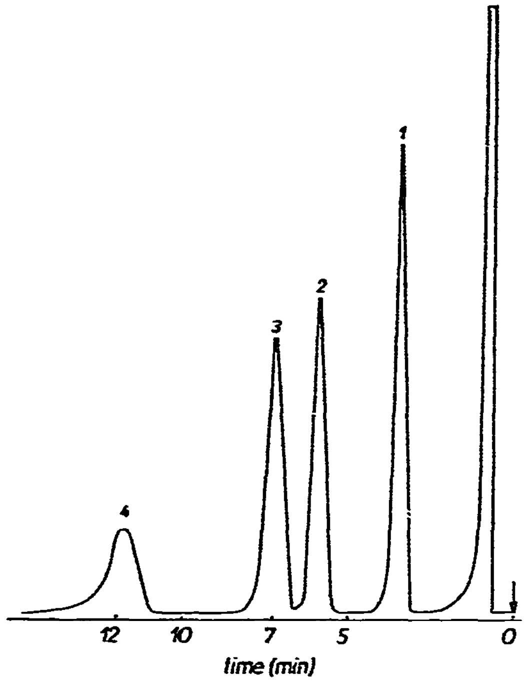


Fig. 2. Chromatogram of standard mixture 3 (see Table III). Stationary phase I; column 1; column temperature, 200°C; carrier gas, argon; flow-rate, 20 cm^3/min. Peaks: 1 = triphenylmethane; 2 = phenanthrene; 3 = anthracene; 4 = carbazole.

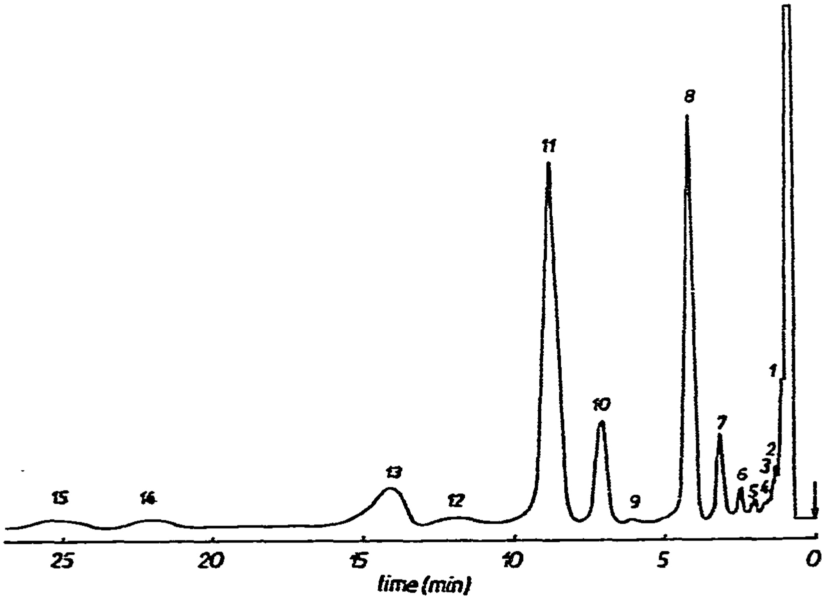


Fig. 3. Chromatogram of commercial anthracene with added triphenylmethane. Stationary phase I; column I; column temperature, 200°C; carrier gas, argon; flow-rate, 20 cm^3/min. Peaks: 1 = naphthalene; 2 = biphenyl; 3 = α- and β-methylnaphthalenes; 4 = dimethylnaphthalenes; 5 = acenaphthene; 6 = diphenyl oxide; 7 = fluorene; 8 = triphenylmethane; 9 = diphenyl sulphide; 10 = phenanthrene; 11 = anthracene; 12 = acridine; 13 = carbazole; 14 = fluoranthene; 15 = pyrene.

anthracene. In samples containing about 60% of anthracene the latter was determined directly, whereas in samples with an anthracene content exceeding 90% only the contaminants were determined, the amount of anthracene being found from the difference from 100%.

Table IV gives the results of the determinations and their evaluation for three standard mixtures and for commercial and chemically pure anthracene. Results similar to those in Table IV have also been obtained for the same samples in two other laboratories were N,N'-bis(*p*-phenylbenzylidene-α,α'-bi-*p*-toluidine)[28,33] was used as the liquid crystalline stationary phase.

TABLE IV

RESULTS OF DETERMINATION AND EVALUATION OF ACCURACY

The calculations are based on ten determinations, except for sample 6 (six determinations).

Sample No.	*Compound determined*	*Actual content (%)*	*Content found (%)*	*Standard deviation (%)*	*Confidence limits (%)*	*Coefficient of variation (%)*
1	Phenanthrene	4.53	4.58	0.088	4.58 ± 0.06	1.92
	Carbazole	5.93	5.98	0.142	5.98 ± 0.10	2.37
2	Phenanthrene	0.35	0.37	0.027	0.37 ± 0.02	7.30
	Carbazole	4.64	4.91	0.436	4.91 ± 0.31	8.88
3	Phenanthrene	23.10	23.12	0.782	23.12 ± 0.56	3.38
	Anthracene	26.55	27.29	1.092	27.29 ± 0.78	4.00
	Carbazole	50.35	51.96	2.029	51.96 ± 1.45	3.98
4	Phenanthrene		9.92	0.167	9.92 ± 0.12	1.68
	Anthracene		46.32	0.844	46.32 ± 0.60	1.82
	Carbazole		12.61	0.321	12.61 ± 0.23	2.54
5	Phenanthrene		0.05	0.007	0.05 ± 0.005	14.9
	Anthracene*		98.84			
	Carbazole		1.11	0.062	1.11 ± 0.04	5.61
6	Phenanthrene		0.42	0.026	0.42 ± 0.03	6.19
	Anthracene*		97.57			
	Carbazole		1.21	0.024	1.21 ± 0.03	1.98
	Fluorene		0.80	0.024	0.80 ± 0.03	3.00

* The contents of anthracene were found by subtraction from 100%.

CONCLUSION

Mixtures of phenanthrene, anthracene and carbazole can be well separated on the liquid crystalline stationary phase I. The separation is so good that it allows the determination of the individual components irrespective of their proportions in the mixture. Triphenylmethane is used as the internal standard.

The determination of contaminants in anthracene has been carried out for phenanthrene and carbazole, and in one instance also for fluorene. The results obtained for carbazole suffer from greater errors than those for phenanthrene. The remaining contaminants that occur in anthracene can also be determined, but they were present in the samples tested in only small amounts.

The possibility of separating and determinating polynuclear aromatic hydrocarbons containing thiophenic sulphur, *e.g.*, in anthracene, was not investigated. These compounds, if they are present in the samples tested, occur in very small concentrations.

Reproducible results were obtained for one column during 6 months. A condition for prolonged operation of a column is the use of a carrier gas with a minimum oxygen content. It has been found that the use of non-deoxygenated nitrogen rapidly results in a considerable decrease in the efficiency of the column.

ACKNOWLEDGEMENTS

We thank Mrs. A. Ziólek for synthesizing I and Mr. J. Dziaduszek for synthesizing II.

REFERENCES

1 E. Luck, *Angew. Chem.*, 16 (1903) 18.

2 Ł. D. Gluzman and L. I. Edelman, *Laboratornyj Kontrol Koksochemiczieskowo Proizwodstwa*, Metallurgizdat, Charkow, 1967, p. 635.

3 J. Jurkiewicz and S. Juzwa, *Koks Smola Gaz*, 7 (1962) 141.

4 W. Smidt, *Brennst.-Chem.*, 33 (1952) 176.

5 J. Ubaldini and V. Crespi, *Ann. Chim. Appl.*, 39 (1949) 77.

6 E. Funakubo, Y. Matsumoto and J. Kavanischi, *Brennst.-Chem.*, 41 (1960) 46.

7 C. Columbic, *Anal. Chem.*, 31 (1949) 1440.

8 D. Ciecierska, K. Gorczyńska and J. Świętosławska, *Przem. Chem.*, 9 (1953) 616.

9 B. J. Butakowa and N. J. Rusjanowa, *Chimiczeskije Produkty Koksowania Uglej Wostoka SSSR*, 3 (1965) 309.

10 L. F. Lipatowa and W. M. Biednow, *Koks Khim.*, No. 9 (1968) 47.

11 P. Srap and W. Utynon, *Appl. Spectrosc.*, 18 (1964) 186.

12 N. A. Kekin and L. M. Kornilowa, *Sb. Tr. Ukr. Khim. Inst.*, 121 (1969) 104.

13 G. Collin and M. Zander, *Erdöl Kohle Erdgas Petrochem.*, 25 (1972) 305.

14 Ł. S. Cebrij, N. D. Chizniak and E. J. Wajl, *Woprosy Technologii Ulawliwanija i Pierierabotki Produktow Koksowania*, No. 3 (1974) 149.

15 T. J. Gornych and A. G. Pozdiejewa, *Z. Prikl. Khim.*, 27 (1954) 118.

16 F. Bertram and N. Kobisch, *Chem.-Ztg. Chem. Appar.*, 91 (1967) 919.

17 G. Biernoth, *J. Chromatogr.*, 36 (1968) 325.

18 R. Tye and Z. Bell, *Anal. Chem.*, 36 (1964) 1612.

19 S. N. Kipot, A. A. Rok and N. A. Kekin, *Koks Khim.*, No. 5 (1980) 44.

20 K. Bhatia, *Anal. Chem.*, 43 (1971) 609.

21 R. L. Lao, R. S. Thomas, H. Oja and L. Dubois, *Anal. Chem.*, 45 (1973) 908.

22 J. Fryčka, *J. Chromatogr.*, 65 (1972) 341.

23 J. Fryčka, *J. Chromatogr.*, 65 (1972) 432.

24 L. J. Maricz, L. L. Poklonskaja, Ł. M. Ganża, F. N. Ambroziewicz and W. J. Borodin, *Koks Khim.*, No. 8 (1978) 32.

25 N. Carugno and S. Rossi, *J. Gas Chromatogr.*, 5 (1967) 103.

26 G. M. Janini, K. Johnston and W. L. Zielinski, Jr., *Anal. Chem.*, 47 (1975) 670.

27 G. M. Janini, G. M. Muschik and W. L. Zielinski, Jr., *Anal. Chem.*, 48 (1976) 809.

28 G. M. Janini, B. Shaikh and W. L. Zielinski, Jr., *J. Chromatogr.*, 132 (1977) 136.

29 W. L. Zielinski, Jr. and G. M. Janini, *J. Chromatogr.*, 186 (1979) 237.

30 J. W. Strand and A. W. Andren, *Anal. Chem.*, 50 (1978) 1508.

31 Z. Witkiewicz and A. Wacławczyk, *J. Chromatogr.*, 173 (1979) 43.

32 J. Dziaduszek, T. Szczuciński, A. Waclawczyk and Z. Witkiewicz, *Biul. Wojsk. Akad. Tech.*, 28, No. 6 (1979) 73.

33 *Bulletin 773A*, Supelco, Bellefonte, PA, 1977.