Determination of Small Amounts of Carbazole in Anthracene by Synchronous Fluorescence Spectrometry

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Synopsis. After converting anthracene into the Diels-Alder adduct by the reaction with maleic anhydride, and converting the adduct into a water-soluble salt by hydrolysis with potassium hydroxide aqueous solution, carbazole is then extracted into 2,2,4-trimethylpentane together with other impurities. Then carbazole can be determined by synchronous fluorescence spectrometry without interference of the impurities.

Since commercially available anthracene contains carbazole as an impurity and its removal from anthracene is relatively difficult, a determination method of carbazole is required. For the determination of small amounts of carbazole in anthracene, several methods have been developed.[1-3] In the present paper separation of carbazole from anthracene and its determination by synchronous fluorescence spectrometry will be described. By this method, carbazole can be determined more rapidly and simply than previous methods. The determination limit is 10 ppm.

Experimental

Reagents. Maleic anhydride was purified by distillation. 2,2,4-Trimethylpentane used was of the "Spectro" grade.

Apparatus. All the measurements of synchronous fluorescence spectra were made on a Hitachi 650-40 fluorescence spectrophotometer equipped with a Hitachi 056 recorder. The spectral bandpass was set at 2 nm. A 150-W Xenon lamp was used as the exciting source. A $10\times10\times45$ mm^3 quartz cell was used. A Torika MA-1 mixer of Japan Torika Corp. was used as a shaker for the extraction.

Procedure. A mixture of 10 mg of the anthracene sample and 1 g of maleic anhydride was fused at 160 °C for 10 min in a 25-ml Kjeldahl flask (short neck) fitted with an air condenser. The reaction mixture was dissolved by adding 10 ml of 3 mol/l potassium hydroxide aqueous solution and heating with occasional shaking. After the solution had been cooled to room temperature, 10 ml of 2,2,4-trimethylpentane was added. The mixture was thoroughly shaken and allowed to stand for a while. The synchronous fluorescence spectrum of the 2,2,4-trimethylpentane phase was measured with a wavelength interval of 5 nm. Carbazole was determined from the intensity at 335 nm obtained by the base line method. As the standard, the synchronous fluorescence intensity of a 0.2 μg/ml carbazole solution was used. The calibration curve was prepared by using carbazole solutions containing 0—0.2 μg per ml.

Results and Discussion

Synchronous Fluorescence Spectrum. For the determination of carbazole, a wavelength interval of 3 nm is suitable under ordinary conditions.[4] For the determination of more minute amounts of carbazole, however, a larger wavelength interval is necessary for enhancement of the signal-to-noise ratio. From the experimental results, a wavelength interval of 5 nm was effective. The synchronous fluorescence spectrum of carbazole is shown in Fig. 1. The spectrum has a maximum at 335 nm.

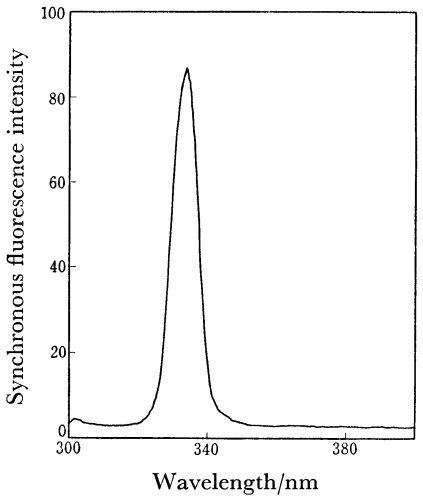

Fig. 1. Synchronous fluorescence spectrum of carbazole. Wavelength interval: 5 nm; solvent: 2,2,4-trimethylpentane.

Removal of Anthracene. The Diels-Alder reaction of anthracene with maleic anhydride was useful for the removal of anthracene as an adduct. Carbazole was separated together with other impurities by extraction into 2,2,4-trimethylpentane after the adduct had been converted into the water-soluble potassium salt by hydrolysis with potassium hydroxide aqueous solution. The Diels-Alder reaction was carried out by fusing the anthracene sample with maleic anhydride. To find the effect of heating time on the reaction, pure anthracene was fused with maleic anhydride by varying the heating time at 160 °C. Table 1 shows the residual amounts of anthracene in the 2,2,4-trimethylpentane phase evaluated by measuring the synchronous fluorescence intensity at 379 nm. Table 1 indicates that the reaction is completed within 5 min. It is recommended, therefore, that the sample is fused at 160 °C for 10 min.

Experiments using saturated hydrocarbons as the medium for the Diels-Alder reaction failed, because maleic anhydride did not dissolve satisfactorily in these solvents having desired boiling points.

Calibration Curve. A calibration curve of carbazole was linear over the concentration range from 0.01 to 0.2 μg/ml. As the standard a 0.2 μg/ml carbazole solution was used, and the coefficient of variation obtained in 20 measurements was 0.73%.

Effects of Impurities in Anthracene. Effects of disturbing substances due to absorption have been reported in the previous paper.[4] Acenaphthene shows the spectral interference, but the determination of a

Table 1. Effect of heating time on Diels-Alder reaction of anthracene with maleic anhydride

Heating time / min	Synchronous fluorescence intensity[a]	Residual amounts of anthracene: Concentration / ng ml^{-1}	Residual amounts of anthracene: Total amounts / ng
3	5.0	14	140
3	18.5	53	530
5	<1.0	<3	<30
5	<1.0	<3	<30
10	<1.0	<3	<30
10	<1.0	<3	<30
15	<1.0	<3	<30

a) As the standard, synchronous fluorescence intensity (wavelength interval=5 nm) at 379 nm of a 0.200 μg/ml anthracene solution was taken as 70 div.

0.2 μg/ml carbazole solution was not interfered with the presence of less than 8-fold amount of acenaphthene.

Determination of Carbazole in Synthetic Mixtures. The analytical results of synthetic mixtures are shown in Table 2, Nos. 1—11. Each mixture contains 0.1% of biphenyl, acenaphthene, fluorene, dibenzofuran, and phenanthrene and 0.01% of perylene, fluoranthene, naphthacene, chrysene, and 9,10-anthraquinone. Table 2, Nos. 1—11 indicate that the analytical results agree well with the contents of carbazole. Therefore, carbazole in anthracene can be determined by the present method.

Determination of Carbazole in Practical Samples. Carbazole in three kinds of commercial anthracene was determined by the present method, and the results were compared with the analytical results obtained by a spectrophotometric method.[1] As is shown in Table 2, Nos. 12—14, both results agree within experimental errors. The synchronous fluorescence spectra of the solutions used for the determination exhibited the characteristic signal of carbazole having a peak at 335 nm. In addition, the solutions did not show the absorption based on interfering impurities. Therefore, the method proposed in the present paper can be applied to practical samples of anthracene. The determination of carbazole by the conventional fluorimetry was unsuccessful because of the interference of other luminescent species.

Table 2. Analytical results for carbazole in synthetic mixtures and practical samples

No.	Content / %	Synchronous fluorescence intensity[a]	Found (%)	
1	0.0010	4.4	0.001_1	
2	0.0040	16.3	0.004_0	
3	0.0080	30.5	0.007_6	
4	0.0120	47.7	0.011_8	
5	0.0160	61.3	0.015_2	
6	0.0200	78.4	0.019_7	
7	0.0200	76.9	0.019_4	$\bar{x}=0.019_6$
8	0.0200	77.5	0.019_5	$\sigma=0.00018$
9	0.0200	77.4	0.019_4	C.V.=0.93%
10	0.0200	79.1	0.019_9	
11	0.0200	78.8	0.019_7	
12	0.021_7	81.8	0.020_4	
13	0.003_0	11.8	0.003_0	
14	0.12_9	48.4[b]	0.12_2	

a) As the standard, the synchronous fluorescence intensity of a 0.200 μg/ml carbazole solution was taken as 80 div. b) Measured after the solution had been diluted 10 times.

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