2254 © 1983 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 56, 2254—2257 (1983) [Vol. 56, No. 8

Simultaneous Determination of Trace Amounts of Carbazole and Anthracene in Dibenzofuran by Synchronous Fluorescence Spectrometry after Zone-melting Separation

Masaki TACHIBANA* and Motohisa FURUSAWA
Faculty of Engineering, Yamanashi University, Takeda, Kofu 400

(Received December 4, 1982)

Trace amounts of carbazole and anthracene in dibenzofuran can be simultaneously determined by measuring the synchronous fluorescence intensities at 336 and 381 nm respectively. The determination limit is 2 ppm. For the application of this method to the practical samples containing interfering impurities, a zone-melting technique was applied successfully to remove the impurities prior to the determination. The recoveries of carbazole and anthracene were 99 and 92% respectively.

Synchronous fluorescence spectrometry was introduced by Lloyd[1)] and has been further developed as a technique for the multicomponent analysis of polynuclear aromatic compounds.[2—5)] In this spectrometry, a fluorescence signal is recorded while both excitation and emission wavelengths are scanned simultaneously with a fixed wavelength interval between them. Consequently, this method offers several advantages compared with conventional fluorimetry, an enhancement in selectivity by a narrowing of the spectral band, and a decrease of spectral interference from other luminescent species.

The determination of small amounts of carbazole and anthracene by ultraviolet spectrophotometry[6)] has been developed. The determination limit is approximately 0.01% and it is difficult to apply to samples containing colored substances. Other spectrophotometric methods[7—8)] have been also developed for the determination of carbazole. The determination limits are more than 0.004%.

In the present paper, simultaneous determination of trace amounts of carbazole and anthracene by synchronous fluorescence spectrometry is described. The determination limit is 2 ppm. Carbazole and anthracene in dibenzofuran can be selectively separated from the impurities by the zone-melting technique because each distribution coefficient is greater than unity. The proposed method, therefore, has a wide applicability to the determination of trace amounts of carbazole and anthracene in the practical samples containing interfering impurities. Due to the zone-melting separation, however, this method requires a relatively large amount of the sample and is time-consuming.

Experimental

Reagents. Commercially available dibenzofuran was dissolved in warm acetic acid and the solution was stirred for a while after the addition of a small amount of chromium trioxide. The crystals precipitated by the addition of water were collected, washed with water, dried, and dissolved in benzene. The benzene solution was shaken 4 times with 85% sulfuric acid, washed with water, dried over anhydrous calcium chloride, and passed through an alumina column, and then the benzene was evaporated off. The dibenzofuran thus obtained was further purified by zone refining. The content of carbazole and anthracene was less than 0.1 ppm. Cyclohexane and xylene were of guaranteed reagent grade and used without further purification.

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 $10\times 10\times 45$ mm^3 quartz cell was used.

For zone melting a Shibayama SS-950 high-speed zone refiner was used. In this apparatus six zones are produced by six ring heaters placed at equal spacings on the charge, and each zone is set to travel by moving the heater along the charge.

Procedure. In a glass tube with an i.d. of 4 mm, 4.0 g of the sample was charged to a length of about 26 cm, and then the zone-pass was repeated 20 times. The molten zones about 30 mm long were set to travel at the speed of 100 mm/h. During the travels, the zones were stirred by spinning the tube at 1200 min^{-1} with reversal of the rotation direction at intervals of 1.0 s. Exactly 2.0 g of the zone-molten sample was cut out from the beginning part of the ingot and dissolved in 50 ml of xylene. Then 2 ml of the solution was transferred into a 20-ml volumetric flask and diluted to the mark with cyclohexane. The synchronous fluorescence intensity of the solution was measured at 336 nm for carbazole and at 381 nm for anthracene with the wavelength interval of 5 nm. As the standard, the synchronous fluorescence intensity of a dibenzofuran solution (0.1 μg/ml) in cyclohexane was used, which was measured at 303 nm with a wavelength interval of 6 nm. The calibration curves for carbazole and anthracene were prepared by using their solutions (0—0.2 μg/ml) containing dibenzofuran (4 mg/ml). Carbazole was almost recovered quantitatively, but the recovery of anthracene was 92%. The incomplete recovery of anthracene was corrected for by using the reciprocal of 0.92 as the correction factor.

Results and Discussion

Synchronous Fluorescence Spectra. A wavelength interval is one of the important factors in the measurement of synchronous fluorescence spectrum. For the determination of carbazole and anthracene, the wavelength interval of 3 nm is suitable under ordinary conditions.[5)] For the determination of more minute amounts of these compounds, however, a larger wavelength interval is necessary for enhancement of the signal-to-noise ratio, and a wavelength interval of 5 nm was effective. The synchronous fluorescence spectrum of a mixed solution containing carbazole (0.2 μg/ml), anthracene (0.2 μg/ml) and dibenzofuran (4 mg/ml) is shown in Fig. 1(1). For comparison, the spectrum of

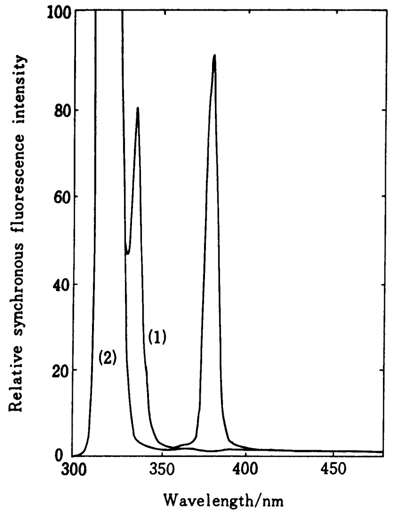

Fig. 1. Synchronous fluorescence spectra of carbazole, anthracene, and dibenzofuran.
Wavelength interval ($\Delta\lambda$): 5 nm; solvent: cyclohexane–xylene mixture (9 : 1); standard: synchronous fluorescence intensity of a dibenzofuran solution (0.100 μg/ml) in cyclohexane measured at 303 nm ($\Delta\lambda = 6$ nm) was taken as 70 div.; (1): dibenzofuran (4.0 mg/ml) containing both carbazole (0.20 μg/ml) and anthracene (0.20 μg/ml); (2): dibenzofuran (4.0 mg/ml).

dibenzofuran solution (4 mg/ml) measured under identical experimental conditions is shown in Fig. 1(2). In Fig. 1 the spectral bands of these compounds are well-resolved, and the peaks at 336 and 381 nm are due to carbazole and anthracene, respectively.

Calibration Curves. For the determination of minute amounts of carbazole and anthracene in dibenzofuran, it is desirable to use a concentrated solution of the sample for the measurement of synchronous fluorescence spectrum. On the other hand, the concentrated solution shows the interferences due to both absorption and fluorescence of dibenzofuran at the characteristic wavelength of carbazole. From the result of experiments the concentration of 4 mg/ml was found suitable. In this concentration, the interference seems to be correctable by using a calibration curve, which is prepared under the presence of dibenzofuran. The calibration curves of carbazole and anthracene were prepared by using their solutions (0—0.2 μg/ml) containing dibenzofuran (4 mg/ml). The synchronous fluorescence intensities of carbazole and anthracene were measured at 336 and 381 nm respectively. As the standard, the synchronous fluorescence intensity of a dibenzofuran solution (0.1 μg/ml) in cyclohexane was used, which was measured at 303 nm with a wavelength interval of 6 nm. The calibration curves thus obtained were linear. However, the curve for carbazole did not pass the origin, and the gradient showed a slight decrease compared with the corresponding curve of carbazole alone.

Separation by Zone-melting Technique. To remove the impurities contained in the practical samples, a zone-melting method was applied. The dibenzofuran sample containing both carbazole (66 ppm) and anthracene (65 ppm) was charged in the tube for the zone melting. The zone-molten ingot obtained was divided into 15 portions. The concentrations of the carbazole and the anthracene were simultaneously measured by the synchronous fluorescence method, and then each relative concentration, C/C_0, was calculated, where C_0 and C were initial and final concentrations, respectively. Their concentration profiles in dibenzofuran are shown in Figs. 2(1) and (2), which indicate that both compounds are concentrated toward the beginning of the zone-molten ingot. The profile for acenaphthene which interferes the determination of carbazole is shown in Fig. 2(3). The initial content of acenaphthene was 0.24%. Acenaphthene was evaluated by ultraviolet spectrophotometry. Figure 2(3) shows that acenaphthene is removed from the beginning of the ingot. Some practical samples of dibenzofuran contain colored substances which show the interference due to absorption, and they were found to be accumulated in the end of the ingot. By these experiments carbazole and anthracene in dibenzofuran were found to be effectively separated from the interfering impurities.

Recoveries of Carbazole and Anthracene. After the zone melting had been performed on the dibenzofuran sample containing carbazole (66 ppm) and anthracene (65 ppm), the zone-molten ingot was divided into 13 portions. The quantities of both compounds in each portion were determined, and the relations between the amounts of the dibenzofuran cut out from the beginning of the ingot and the recoveries of both compounds were calculated. The results illustrated in Fig. 3 indicate that the use of 2.0 g of the zone-molten ingot was preferable for the determination judging from the recoveries of both compounds and the removal of the interfering impurities. Approximately 100% of carbazole and 92% of anthracene are recovered. To measure the recoveries more precisely, the zone melting was

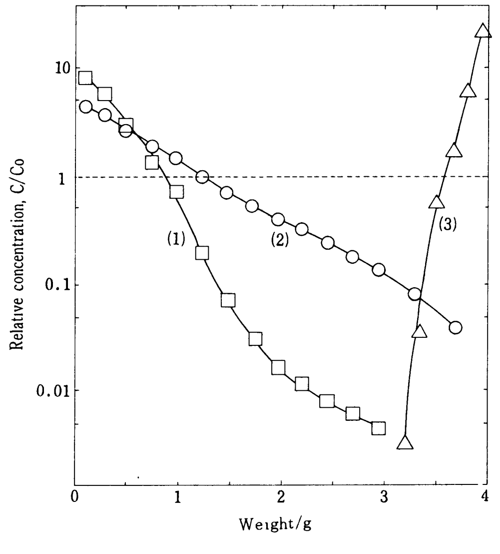

Fig. 2. Concentration profiles for carbazole, anthracene, and acenaphthene in dibenzofuran.
C_0 and C are initial and final contents of the solute; (1): carbazole, $C_0 = 66$ ppm; (2): anthracene, $C_0 = 65$ ppm; (3): acenaphthene, $C_0 = 0.24\%$.

TABLE 1. RECOVERIES OF CARBAZOLE AND ANTHRACENE

Added (μg)		Found (μg)		Recovery %			
Carbazole	Anthracene	Carbazole	Anthracene	Carbazole		Anthracene	
265	282	265	261	$100._0$	$\bar{x}=99._1$ $\sigma=1.2$ C.V.$=1.2\%$	$92._6$	$\bar{x}=92._1$ $\sigma=0.92$ C.V.$=1.0\%$
265	282	263	260	$99._2$		$92._2$	
265	282	268	264	$101._1$		$93._6$	
169	191	167	177	$98._8$		$92._7$	
93.4	101	92.0	91.6	$98._5$		$90._7$	
59.9	70.7	59.6	65.6	$99._5$		$92._8$	
59.9	70.7	59.1	64.5	$98._7$		$91._2$	
29.9	29.9	28.9	27.3	$96._7$		$91._3$	

TABLE 2. ANALYTICAL RESULTS FOR CARBAZOLE AND ANTHRACENE IN SYNTHETIC MIXTURES

Content ppm		Relative synchronous fluorescence intensity[a)]		Found ppm	
Carbazole	Anthracene	Carbazole	Anthracene	Carbazole	Anthracene
1.9	1.9	6.2	5.7	$2._1$	$1._7$
3.8	3.8	11.2	12.2	$3._7$	$3._6$
7.5	8.8	22.9	29.2	$7._6$	$8._6$
11.7	12.6	36.2	43.1	$11._9$	$12._5$
21.5	24.2	66.2	84.0	$22._0$	$24._8$
3.1	22.8	9.4	78.6	$3._1$	$23._2$
18.2	3.5	54.4	11.4	$18._1$	$3._4$
32.8	36.3	51.8[b)]	61.4[b)]	$33._8$	$36._3$
48.4	52.7	74.0[b)]	87.2[b)]	$48._3$	$51._5$

a) Synchronous fluorescence intensity of the dibenzofuran solution (0.100 μg/ml) in cyclohexane measured at 303 nm (wavelength interval = 6 nm) was taken as 70 div. b) 2 mg/ml solution of the mixture was used for the measurement.

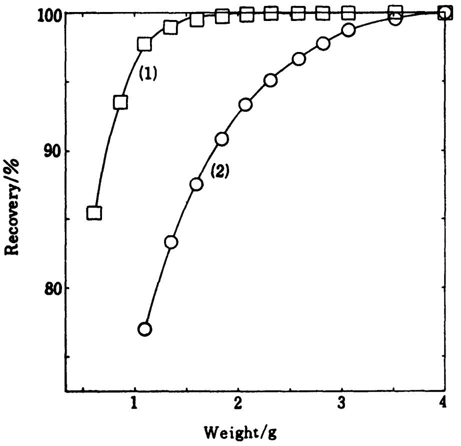

Fig. 3. Recovery profiles for carbazole and anthracene. (1): Carbazole, $C_0=66$ ppm; (2): anthracene, $C_0=65$ ppm.

carried out by the use of the dibenzofuran samples containing various amounts of both compounds. The quantities of both compounds in a 2.0 g portion of the zone-molten ingot are shown in Table 1. The recoveries of carbazole and anthracene are 99% with a coefficient of variation of 1.2%, and 92% with that of 1.0%, respectively. Carbazole can be almost quantitatively recovered, but anthracene cannot. The incomplete recovery of anthracene, however, can be corrected for by use of the reciprocal of 0.92 as the correction factor because a reproducible value is obtained.

Determination of Carbazole and Anthracene in Synthetic Mixtures. The analytical results for carbazole and anthracene in synthetic mixtures of dibenzofuran are shown in Table 2. Each mixture contains 0.3% of biphenyl, naphthalene, acenaphthene, fluorene, and phenanthrene, and 0.02% of pyrene, fluoranthene, 9-fluorenone, 1,4-naphthoquinone, and 9,10-phenanthrenequinone. Table 2 indicates that the analytical results agree closely with the individual contents of carbazole and anthracene in the synthetic mixtures. Therefore, trace amounts of carbazole and anthracene in dibenzofuran containing impurities can be simultaneously determined by the present method.

Determination of Carbazole and Anthracene in Practical Samples. Carbazole and anthracene in three different commercial dibenzofuran samples were determined by the present method. The analytical results for carbazole were 61, 41, and 12 ppm, and those for anthracene, 65, 41, and 24 ppm, respectively. The shapes of the synchronous fluorescence spectra, one of which is shown in Fig. 4(1), agree closely with that of the spectrum shown in Fig. 1(1). The solutions used for the determination did not show the absorption based on interfering impurities. The synchronous fluorescence spectra of the remaining parts of the zone-molten ingot of the practical samples were also measured by the same procedure. From these spectra, one of which is shown in Fig. 4(2), the interfering impurities in dibenzofuran are found to be accumulated toward the end of the zone-molten ingot. As the results of the above experi-

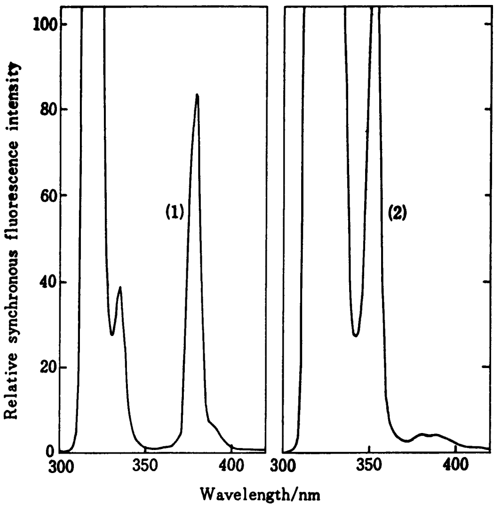

Fig. 4. Synchronous fluorescence spectra of zone-molten commercial dibenzofuran.

$\Delta\lambda$: 5 nm; solvent: cyclohexane–xylene mixture (9 : 1); standard: synchronous fluorescence intensity of a dibenzofuran solution (0.100 μg/ml) in cyclohexane measured at 303 nm ($\Delta\lambda$=6 nm) was taken as 70 div.; (1): solution used for the determination, 4.0 mg/ml; (2): solution prepared by dissolving the opposite end of the same ingot, 4.0 mg/ml.

ments, the method proposed in the present paper can be applied to the practical samples of dibenzofuran.

The authors are indebted to Miss Sumiko Yamada and Mr. Tadayuki Yano for their technical assistance. The present work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

References

1) J. B. F. Lloyd, *Nature* (*London*), *Phys. Sci.*, **231**, 64 (1971).
2) Tuan Vo-Dinh, *Anal. Chem.*, **50**, 396 (1978).
3) Tuan Vo-Dinh, R. B. Gammage, and P. R. Martinez, *Anal. Chem.*, **53**, 253 (1981).
4) T. Katoh, S. Yokoyama, and Y. Sanada, *Fuel*, **59**, 845 (1980).
5) M. Furusawa, M. Tachibana, and Y. Hayashi, *Bunseki Kagaku*, **31**, 229 (1982).
6) K. Kihara, *Bunseki Kiki*, **11**, 436 (1973).
7) M. Furusawa, S. Yamada, M. Tachibana, and T. Natori, *Yamanashi Daigaku Kohgakubu Kenkyu Hohkoku*, **28**, 142 (1977).
8) M. Furusawa, M. Tachibana, S. Yamada, and Y. Ishida, *Bunseki Kagaku*, **28**, 130 (1979).