# The Separation by Means of the Zone-melting Technique and the Spectrofluorometric Determination of Trace Amounts of Anthracene in Phenanthrene

Motohisa FURUSAWA* and Masaki TACHIBANA
*Faculty of Engineering, Yamanashi University, Takeda, Kofu 400*
(Received December 16, 1980)

Since ordinarily available phenanthrene contains interfering impurities, such as phenanthrenequinone and fluoranthene, it is difficult to determine anthracene by spectrofluorimetry directly. Trace amounts of anthracene in phenanthrene can, however, be selectively separated from the interfering impurities by means of the zone-melting technique, for the distribution coefficient of anthracene in phenanthrene is greater than unity. The anthracene thus separated is spectrofluorometrically measured using xylene as the solvent. The determination limit of anthracene is 0.05 ppm. In a glass tube with an i.d. of 4 mm, 4.0 g of the sample was charged to a length of about 27 cm, and then the zone-pass was repeated 20 times. The molten zones were set to travel at a speed of 100 mm/h under constant stirring. Exactly 2.5 g of the zone-molten sample was cut out and dissolved in 50 ml of xylene. The fluorescence intensity of the solution was measured at 403 nm with excitation at 378 nm. The recovery of anthracene was 95%, with a coefficient of variation of 0.6%. The incompleteness of the recovery was corrected for.

The fluorometric determination of trace amounts of anthracene in phenanthrene has been developed by Parker *et al.*[1] and Iwashima *et al.*[2] These methods, however, are difficult to apply to the determination of anthracene in ordinarily available samples of phenanthrene, for these samples contain interfering impurities, such as fluoranthene and phenanthrenequinone.

In the present paper, the separation of anthracene from the interfering impurities in phenanthrene by means of the zone-melting technique and its spectrofluorometric determination will be described. The distribution coefficient of anthracene in phenanthrene being greater than unity, anthracene is concentrated toward the beginning of the ingot by repeating the zone-melting process. On the contrary, the interfering impurities show an opposite behavior; they are accumulated toward the end of the ingot. Therefore, the anthracene can be separated. The anthracene thus separated is spectrofluorometrically measured, using xylene as the solvent. The determination limit of anthracene is 0.05 ppm.

## Experimental

*Reagent.* Phenanthrene was purified in the following manner. Commercial phenanthrene was fused with maleic anhydride in the presence of chloranil at 170 °C for 1 h to remove the anthracene. After cooling, the solidified product was dissolved in acetone. Phenanthrene crystals were precipitated by the addition of water, collected, and dissolved in benzene. The solution was shaken with 85% sulfuric acid, and then the benzene was evaporated. After this process had been repeated once more, the phenanthrene thus obtained was further purified by repeating the zone refining according to the method of Matsumoto *et al.*[3] and finally by ordinary zone refining.

*Apparatus.* The fluorometric measurements were carried out using a Hitachi 204 fluorescence spectrophotometer. A 150-W xenon lamp was used as the exciting source. A 10 mm × 10 mm × 45 mm quartz cell was used.

Zone melting was performed using a Shibayama SS-950 high-speed zone refiner. 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. After traveling to the distance between the centers of the nearest neighbor zones, the heater assembly returns quickly to its initial position. In this cycle, each molten zone is transferred into its next one. The tube is rotated around its longitudinal axis with a reversal of the rotation direction.

*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 27 cm, and then the zone-pass was repeated 20 times. The molten zones about 30 mm in length were set to travel at a speed of 100 mm/h. During the travels, the zones were stirred by spinning the glass tube at 1200 rpm with a reversal of the rotation direction at intervals of 1.0 s. Exactly 2.5 g of the zone-molten sample was cut out from the beginning part of the ingot and dissolved in 50 ml of xylene. The fluorescence intensity of the solution was measured at 403 nm, with excitation at 378 nm. An anthracene solution (50 or 500 ng/ml) and xylene were used as the standard and the blank respectively. The quantity of anthracene was determined by using a calibration curve, which had been prepared by measuring the relative fluorescence intensities of anthracene solutions (0—50 or 0—500 ng/ml) containing phenanthrene (50 mg/ml). Since the recovery of anthracene was 95%, the incompleteness of the recovery was corrected for by using the reciprocal of 0.95 as the correction factor.

## Results and Discussion

*Solvent.* Fluorometric methods for the determination of trace amounts of anthracene in phenanthrene[1,2] use ethanol as the solvent, and the lower limit of determination in these methods is approximately 1 ppm. For the determination of more minute amounts of anthracene in phenanthrene, it is desirable to measure the fluorescence intensity of anthracene using a concentrated solution of the sample. For the purpose of dissolving large amounts of phenanthrene, xylene was selected as the solvent.

*Fluorescence Spectra.* The fluorescence spectra of anthracene and phenanthrene were measured with excitation at 378 nm by means of an apparatus with the same sensitivity. The measurements were made on a

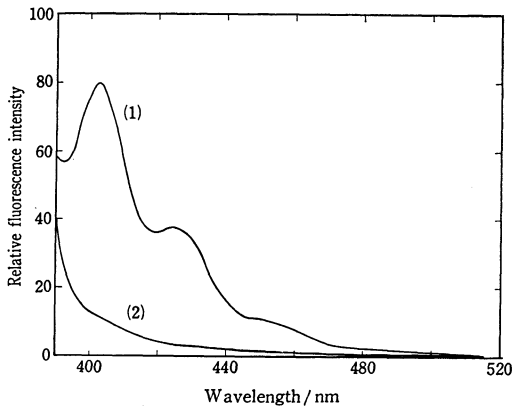


Fig. 1. Fluorescence emission spectra of anthracene and phenanthrene.
Excitation wavelength: 378 nm; solvent: xylene; (1): anthracene (uncorrected), 50 ng/ml; (2): Phenanthrene (uncorrected), 50 mg/ml.

solution containing 50 ng/ml of anthracene and on a concentrated phenanthrene solution containing a concentration $10^6$ times as high as that of anthracene. These spectra are shown in Fig. 1. The fluorescence spectrum of anthracene exhibits a maximum at 403 nm. A concentrated solution of phenanthrene shows a weak fluorescence at this characteristic wavelength of anthracene.

*Calibration Curves.* For the determination of trace amounts of anthracene in phenanthrene, it is necessary to correct for the influence of phenanthrene. The fluorescence intensity of phenanthrene at the characteristic wavelength of anthracene is so weak that it seems to be correctable by using a calibration curve, which can be prepared by measuring the fluorescence intensities of anthracene solutions containing phenanthrene. The sensitivity of the fluorescence spectrophotometer was adjusted by setting the intensity of a standard anthracene solution (50 or 500 ng/ml) at 80 division; then, the relative fluorescence intensities of anthracene solutions (0—50 and 0—500 ng/ml) containing phenanthrene (50 mg/ml) were measured. The resultant calibration curves are shown in Figs. 2(1) and (2). For comparison, the fluorescence intensities of anthracene solutions were also measured in the absence of phenanthrene; the results are illustrated in Figs. 2(3) and (4). As a result of the influence of phenanthrene, the calibration curves shown in Figs. 2(1) and (2) do not intersect at the point of origin, and each gradient shows a slight decrease compared with the corresponding curve of anthracene alone. However, good linear relationships are observed between the fluorescence intensity and the concentration of anthracene. Therefore, the influence of phenanthrene is correctable by using the calibration curve, and anthracene in phenanthrene can be determined over the range from 0.05 to 10 ppm.

*Separation of Anthracene.* Since ordinarily available phenanthrene contains interfering impurities, such as phenanthrenequinone and fluoranthene, it is necessary to separate anthracene prior to its determination. For this purpose, the separation of anthracene by means of the zone-melting technique was studied. After the zone melting had been performed using phenanthrene samples containing 1.7 and 12.3 ppm of anthracene, each zone-molten ingot was divided into fifteen portions 1.5—2 cm in length, and then the anthracene was spectrofluorometrically measured. The resultant distribution profile of anthracene on the zone-molten ingot is shown in Fig. 3(1). The distribution profiles of phenanthrenequinone and fluoranthene, obtained in a manner similar to that used for anthracene, are shown in Figs. 3(2) and (3). The initial contents of phenanthrenequinone and fluoranthene were 0.1% and 0.2% respectively. The phenanthrenequinone was spectrophotometrically evaluated by employing the absorption at 416 nm, using a mixture of xylene and methanol (1 : 1) as the solvent. The presence of methanol was necessary to avoid a decrease in the absorbance. The fluoranthene was evaluated by measuring the fluores-

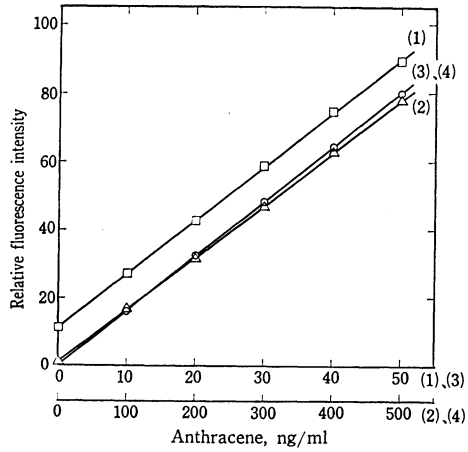


Fig. 2. Calibration curves of anthracene.
(1), (3): As the standard, fluorescence intensity of 50 ng/ml anthracene solution was taken as 80 div.; (2), (4): 500 ng/ml solution was taken as 80 div.; (1), (2): coexistence of phenanthrene, 50 mg/ml; (3), (4): Anthracene alone.

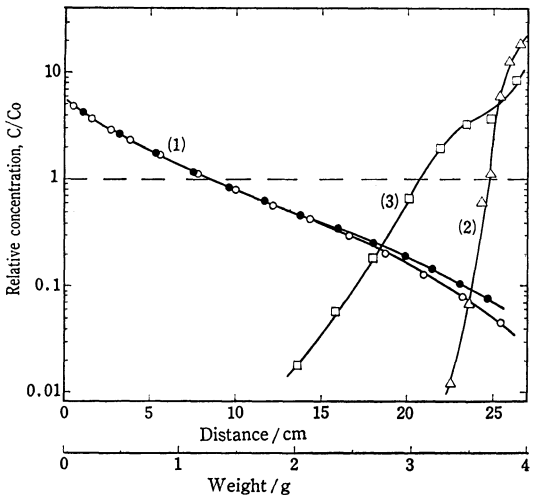


Fig. 3. Concentration profiles for anthracene, phenanthrenequinone and fluoranthene in phenanthrene.
$C_0$ and $C$ are initial and final contents of the solute; (1): anthracene, ○ $C_0=12.3$ ppm, ● $C_0=1.7$ ppm; (2): phenanthrenequinone, $C_0=0.1\%$; (3): fluoranthene, $C_0=0.2\%$.

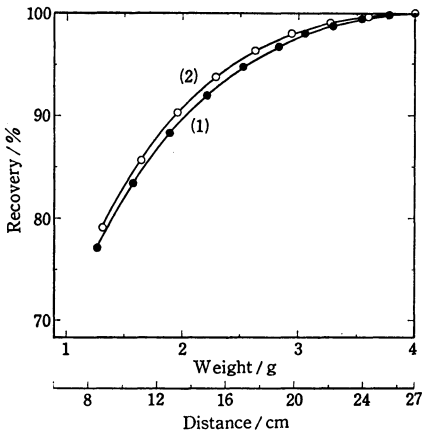


Fig. 4. Recovery profiles for anthracene.
(1): $C_0$=1.7 ppm; (2): $C_0$=12.3 ppm.

cence intensity at 460 nm with excitation at 378 nm, using xylene as the solvent. Figure 3 indicates that anthracene is concentrated toward the beginning of the zone-molten ingot, and that both impurities are effectively removed from the beginning, and accumulated toward the end, of the ingot. Therefore, anthracene in phenanthrene can be effectively separated from these interfering impurities.

*Recovery of Anthracene.* After the zone melting of two phenanthrene samples containing 1.7 and 12.3 ppm of anthracene had been carried out, each zone-molten ingot was divided into 10—12 portions; the quantity of anthracene in each divided ingot was then spectrofluorometrically evaluated. From the results, the relation between the amounts of the ingot cut out from the beginning and the recovery of anthracene were calculated; they are illustrated in Fig. 4. Figures 3 and 4 show that it is the most suitable for the determination of anthracene to use 2.5 g of the sample cut out from the beginning of the ingot. In this case, about 95% of anthracene can be recovered. Under these conditions, the recovery of anthracene was measured more precisely. After the zone melting of the phenanthrene samples had been performed, exactly a 2.5 g portion of each zone-molten ingot was cut out and the quantity of the anthracene was evaluated. The results are shown in Table 1. Table 1 indicates that the recovery is 95%, with a coefficient of variation of 0.6%. Since a reproducible value is obtained, the incompleteness of the recovery can be corrected for by using the reciprocal of 0.95 as the correction factor.

TABLE 1. RECOVERY OF ANTHRACENE

| Anthracene added (μg) | Anthracene found (μg) | Recovery % | |
|---|---|---|---|
| 7.00 | $6.6_3$ | $94._7$ | $\bar{x}=95._1$ $\sigma=0.61$ c. v.=0.6% |
| 7.00 | $6.6_2$ | $94._6$ | |
| 7.00 | $6.7_3$ | $96._1$ | |
| 13.4 | $12._8$ | $95._5$ | |
| 17.2 | $16._2$ | $94._2$ | |
| 25.2 | $23._9$ | $94._8$ | |
| 49.2 | $47._0$ | $95._5$ | |

*Determination of Anthracene in Synthetic Mixtures.* The analytical results for anthracene in synthetic mixtures of phenanthrene are shown in Table 2. Each synthetic mixture contains 200 ppm of phenanthrenequinone, carbazole, and fluorene, 100 ppm of acenaphthene, dibenzofuran, and naphthalene, 40 ppm of 9-fluorenone, and 10 ppm of fluoranthene, pyrene, and anthraquinone. Table 2 indicates that the analytical results agree closely with the individual contents of anthracene in synthetic mixtures. Therefore, trace amounts of anthracene in phenanthrene containing impurities can be determined by this proposed method.

*Determination of Anthracene in Practical Samples.* A commercial sample of phenanthrene containing about 300 ppm of anthracene was purified by treating it with sulfuric acid to remove the anthracene according to the

TABLE 2. ANALYTICAL RESULTS FOR ANTHRACENE IN SYNTHETIC MIXTURES

| No. | Content ppm | Relative fluorescence intensity | Found ppm | |
|---|---|---|---|---|
| 1 | 0.049 | 17.9 | $0.05_6$ | |
| 2 | 0.102 | 24.3 | $0.11_0$ | |
| 3 | 0.385 | 58.2 | $0.39_4$ | |
| 4 | 3.36 | 40.5 | $3.3_4$ | |
| 5 | 6.29 | 74.9 | $6.2_8$ | |
| 6 | 0.644 | 88.7, 88.4 | $0.65_0$, $0.64_7$ | $\bar{x}=0.64_9$ |
| | | 89.5, 89.2 | $0.65_6$, $0.65_4$ | $\sigma=0.0066$ |
| | | 87.1, 89.1 | $0.63_6$, $0.65_3$ | c.v.=1.0% |

Nos. 1—3,6: as the standard, the fluorescence intensity of a 50 ng/ml anthracene solution in xylene was taken as 80 div.; Nos. 4, 5: a 500 ng/ml anthracene solution was used.

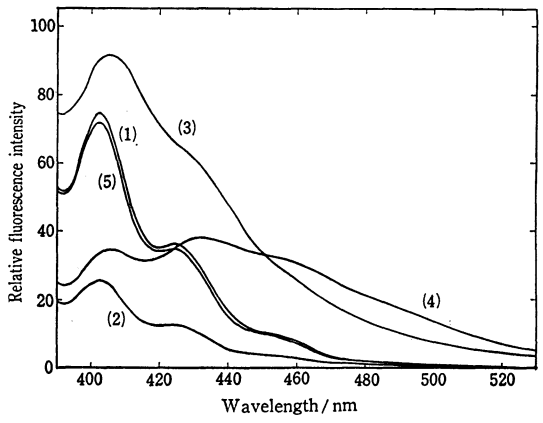


Fig. 5. Comparison of fluorescence emission spectra of practical or zone-molten samples with the spectrum of anthracene containing phenanthrene.
Standard: fluorescence intensity of 1 μg/ml anthracene solution was taken as 80 div; (1), (2): solutions employed for the determination (uncorrected), 50 mg/ml; (3), (4): solutions of practical samples (uncorrected), 100 mg/ml; (5): anthracene solution containing 50 mg/ml of phenanthrene (uncorrected); (1), (3): results of a sample purified with sulfuric acid; (2), (4): results of a sample purified with maleic anhydride and by recrystallization; excitation wavelength: 378 nm; solvent: xylene.

method of Lamey and Maloy.[4] Another commercial phenanthrene containing about 1200 ppm of anthracene was purified by a combination of the treatment with maleic anhydride and recrystallization. Trace amounts of anthracene in the two purified samples were determined by this proposed method. The analytical results were 13 ppm and 4.3 ppm respectively. The fluorescence spectra of the xylene solutions employed for the determination are shown in Figs. 5 (1) and (2). The spectra of the sample solutions were also measured; they are shown in Figs. 5 (3) and (4). The spectrum of an anthracene solution containing phenanthrene is shown in Fig. 5 (5). The shapes of the spectra shown in Figs. 5 (3)—(5) are not identical. However, the shapes of the spectra shown in Figs. 5 (1) and (2) agree closely with that of the spectrum shown in Fig. 5 (5). Therefore, this proposed method can be used in the determination of trace amounts of anthracene in practical samples of phenanthrene.

The authors are indebted to Mrs. Suzuko Kiba and Miss Sumiko Yamada 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) C. A. Parker, C. G. Hatchard, and T. A. Joyce, *Analyst*, **90**, 1 (1965).
2) S. Iwashima, T. Sawada, H. Honda, M. Kuramachi, and J. Aoki, *Bunseki Kagaku*, **25**, 29 (1976).
3) T. Matsumoto, M. Sato, S. Hirayama, and S. Uemura, *Bunseki Kagaku*, **21**, 1641 (1972).
4) S. C. Lamey and J. T. Maloy, *Sep. Sci.*, **9**, 391 (1974).