Zone-Melting Separation of Carbazole and Anthracene from Polynuclear Aromatic Compounds Using Biphenyl as a Medium, Followed by the Synchronous Fluorometric Determination

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

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Biphenyl is favorable as a zone-melting medium for the selective separation of small amounts of carbazole and anthracene and a subsequent determination. A definite amount (20—100 mg) of an aromatic sample was mixed with 4 g of purified biphenyl. The mixture was zone-melted 20 times. The two analytes were accumulated in the beginning part of the zone-molten ingot, but many others were eliminated from the part. After being dissolved in xylene along with the biphenyl, carbazole and anthracene could be simultaneously determined up to 10 ng ml^{-1} by measuring the synchronous fluorescence intensities at 340 and 384 nm, respectively.

Carbazole and anthracene, widely known as constituents of coal tar, can be easily found as chief impurities in many kinds of polynuclear aromatic chemicals. These two materials may, therefore, serve as significant criteria for the purity and the origin of the products made from tar. However, it is difficult to separate and determine small amounts because of the diversity and complexity of these chemicals. Although conventional chromatographic methods are effective for the general separation of a large number of polynuclear aromatic compounds, a selective and simple method for the separation of carbazole and/or anthracene in such products is of great importance.

In the initial investigation, the authors found that the two materials in dibenzofuran are unusually concentrated in the beginning part of the ingot purified by zone melting, and that they can be selectively separated from many other analogs which are normally accumulated in the end part. Consequently, after zone melting both impurities in dibenzofuran could be simultaneously determined by synchronous fluorescence spectrometry without interference of the concomitants.[1] The advanced technique using dibenzofuran as a zone-melting medium could be applied to the determination of small amounts of anthracene in several chemicals, such as fluoranthene,[2] pyrene, anthraquinone, etc.[3] Carbazole in these chemicals, however, could not be determined because of the spectral interference of a large amount of dibenzofuran.

In the present paper the zone-melting technique was further developed by using biphenyl as an alternative medium. Since biphenyl possesses an unusual zone-melting property similar to that of dibenzofuran, carbazole and anthracene can be separated from the analogs in a similar manner. In addition, biphenyl has no effect on the synchronous measurement of carbazole since it fluoresces in a shorter wavelength region than dibenzofuran. Therefore, the two analytes separated by the zone-melting technique could be simultaneously determined by subsequent synchronous fluorimetry. In terms of the separation efficiency for anthracene, however, the biphenyl medium is not as good as the dibenzofuran medium.

Experimental

Reagents. Biphenyl was purified from commercial chemicals in the same manner as dibenzofuran: the procedure was described in detail in a previous paper.[2] Some polynuclear aromatic compounds were purified in the same way as that employed in the initial investigation.[2,3] The others were either zone-refined or used without purification. Xylene of guaranteed reagent grade was used as a solvent without further purification.

Apparatus. A new-type Shibayama SS-950 high-speed zone refiner was used for any zone-melting procedure. The new-model apparatus is identical, except for the length of the molten zone, in mechanism with the old one.[4] All measurements of the synchronous fluorescence spectra were made on a Hitachi 650-40 fluorescence spectrophotometer equipped with a Hitachi 056 recorder. The excitation and emission spectral bandpasses were always set at 2 nm. A 150-W xenon lamp was used as the excitation light source. Quartz cells of 1.00 cm in path length were used.

Zone-Melting Procedure. A definite amount (20—100 mg) of a sample was mixed with 4 g of the purified biphenyl. The mixture was charged in a glass tube of 4-mm i.d. having a silicone rubber stopper. The tube was then mounted vertically in the zone-melting apparatus. Six molten zones, each approximately 40 mm long, were produced by six ring heaters placed at equal spacings on the charge. The zones were set to travel upward at a speed of 100 mm h^{-1}, and the pass was repeated 20 times. During the travel, the zones were stirred by spinning the tube at 20 s^{-1}, with a reversal of the rotation direction at intervals of 1.0 s.

Synchronous Fluorescence Spectrometry. The zone-molten ingot was cut exactly into quarters. The lower half of the ingot was used for a simultaneous determination, the lowest quarter being for the determination of carbazole alone: the half or the quarter was dissolved in 20 ml or 10 ml of xylene. The synchronous fluorescence spectrum of the solution was measured with a wavelength interval of 6 nm. Carbazole and anthracene were determined from the intensities at 340 and 384 nm, respectively, by using the baseline method. The intensities of the two analytes in a xylene solution (both 0.200 μg ml^{-1}) were used as the standard. Both calibration curves were prepared from their xylene solutions. The incomplete recovery of anthracene was finally corrected for.

Results and Discussion

Zone-Melting Behavior in Biphenyl. Zone-melting samples for polynuclear aromatic compounds of interest were prepared by uniformly mixing small amounts of the individual compounds with the purified biphenyl. After all these samples were zone-melted under the same conditions, the variation in the concentration of particular compounds was measured for each portion of the ingot cut into segments. The relative concentration, C/C_0, was subsequently calculated from the result, where C_0 and C are the initial and final concentrations in the biphenyl, respectively. In addition, the results of these calculations were embodied in the form of a concentration profile. The resulting profiles for carbazole and anthracene are shown in Fig. 1, and the profiles for 14 different aromatic compounds are shown in Fig. 2 (A)—(N). Figure 1 indicates that carbazole and anthracene are concentrated toward the beginning part of the zone-molten ingot. On the other hand, Fig. 2 shows that all of the analogs, which have large effects on the spectrofluorometric determination of carbazole and/or anthracene, are accumulated in the end part of the ingot, and that the extent of the accumulation is dependent on not only the species but also the content. With regard to these interfering compounds, except 5*H*-benzo[*b*]carbazole (5*H*-BC), roughly speaking, the zone-melting behavior in biphenyl was similar to that in dibenzofuran. Only the accumulation of 5*H*-BC was reversed by this biphenyl medium. The behavior of these substances indicates that the use of biphenyl as the zone-melting medium is suitable, like dibenzofuran, for the selective separation of carbazole and anthracene from the interfering analogs.

Separation of Carbazole and Anthracene from Interfering Compounds. Judging from Figs. 1 and 2, carbazole and anthracene can be separated from 20 to 100 mg of the interfering compounds, except for naphthacene and 5*H*-BC, when 4 g of biphenyl is used as the medium. It is possible to separate the two analytes from less than about 800 μg of naphthacene, but impossible to separate them from 5*H*-BC completely. The recoveries of carbazole and anthracene in the

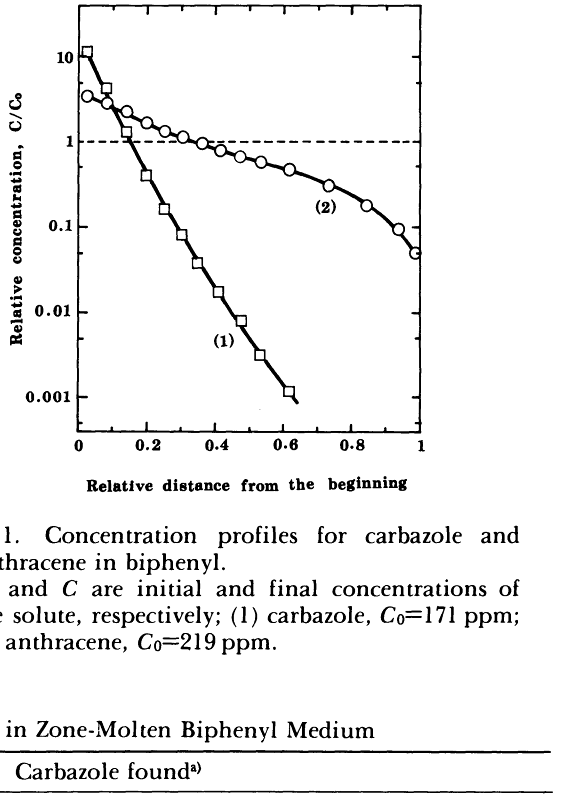

Fig. 1. Concentration profiles for carbazole and anthracene in biphenyl.
C_0 and C are initial and final concentrations of the solute, respectively; (1) carbazole, C_0=171 ppm; (2) anthracene, C_0=219 ppm.

Table 1. Recovery of Carbazole at Various Positions in Zone-Molten Biphenyl Medium

Substances added/mg	Carbazole found[a]					
	0—0.25[b]		0.25—0.5[b]		0.5—0.625[b]	
	Amount	Recovery	Amount	Recovery	Amount	Recovery
	μg	%	μg	%	μg	%
None	2.0_5	$99._5$	0.0_1	$0._5$	0.0_0	$0._0$
None	2.0_4	$99._0$	0.0_1	$0._5$	0.0_0	$0._0$
None	2.0_5	$99._5$	0.0_1	$0._5$	0.0_0	$0._0$
None	2.0_5	$99._5$	0.0_1	$0._5$	0.0_0	$0._0$
9-Fluorenone 22	2.0_6	$100._0$	0.0_1	$0._5$	0.0_0	$0._0$
Anthraquinone 21	2.0_6	$100._0$	0.0_1	$0._5$	—[c]	—
9,10-Phenanthrenequinone 23	2.0_7	$100._5$	0.0_1	$0._5$	0.0_0	$0._0$
Fluoranthene 21	2.0_8	$101._0$	0.0_1	$0._5$	0.0_0	$0._0$
Pyrene 22	2.0_2	$98._1$	0.0_1	$0._5$	0.0_0	$0._0$
Chrysene 21	2.0_6	$100._0$	0.0_2	$1._0$	0.0_0	$0._0$
9-Fluorenone 103	2.0_5	$99._5$	0.0_1	$0._5$	0.0_0	$0._0$
Acenaphthene 101	2.0_3	$98._5$	0.0_1	$0._5$	—[c]	—
Fluoranthene 101	2.1_5	$104._4$	0.0_1	$0._5$	—[c]	—
Fluoranthene 103	2.0_5	$99._5$	0.0_1	$0._5$	—[c]	—
Pyrene 103	2.0_2	$98._1$	0.0_1	$0._5$	0.0_0	$0._0$

a) The total amount of carbazole added to the medium was 2.06 μg. b) These values represent relative distances from the beginning of zone-molten ingot. c) It was impossible to evaluate the amount because of imperfection of the separation.

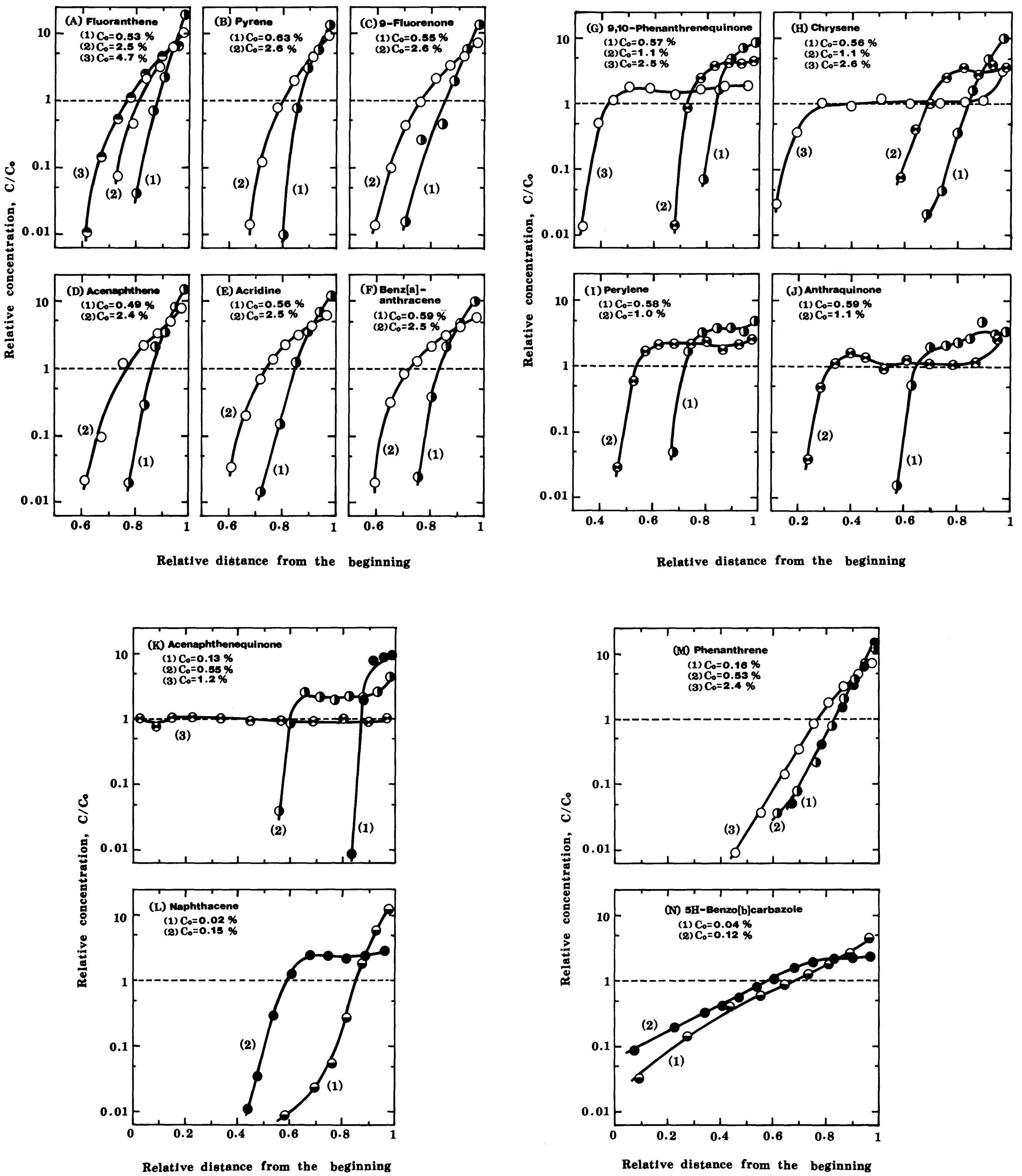

Fig. 2. Concentration profiles for 14 different polynuclear aromatic compounds in biphenyl.

zone-molten fraction of 0—0.25, 0.25—0.5, and 0.5—0.625, where the figures represent the relative distance from the beginning, are summarized as Tables 1 and 2, respectively. As is shown in Table 1, carbazole can be almost quantitatively recovered in the first quarter, even in the presence of a variety of interfering compounds. On the other hand, the recoveries of anthracene in 0—0.25, 0—0.5, and 0—0.625 range from

Table 2. Recovery of Anthracene at Various Positions in Zone-Molten Biphenyl Medium

Substances added/mg		Anthracene found[a)]					
		0—0.25[b)]		0.25—0.5[b)]		0.5—0.625[b)]	
		Amount	Recovery	Amount	Recovery[d)]	Amount	Recovery[d)]
		μg	%	μg	%	μg	%
None		1.5_4	$62._9$	0.5_6	$22._9/85._7$	0.1_5	$6._1/91._8$
None		1.6_4	$66._9$	0.5_3	$21._6/88._6$	0.1_2	$4._9/93._5$
None		1.6_1	$65._7$	0.5_6	$22._9/88._6$	0.1_3	$5._3/93._9$
None		1.6_2	$66._1$	0.5_4	$22._0/88._2$	0.1_4	$5._7/93._9$
9-Fluorenone	22	1.6_2	$66._1$	0.5_0	$20._4/86._5$	0.1_3	$5._3/91._8$
Anthraquinone	21	1.5_6	$63._7$	0.5_5	$22._4/86._1$	0.1_3	$5._3/91._4$
9,10-Phenanthrenequinone	23	1.6_0	$65._3$	0.5_4	$22._0/87._3$	0.1_3	$5._3/92._7$
Fluoranthene	21	1.6_4	$66._9$	0.5_1	$20._8/87._8$	0.1_3	$5._3/93._1$
Pyrene	22	1.5_9	$64._9$	0.5_2	$21._2/86._1$	0.1_4	$5._7/91._8$
Chrysene	21	1.5_8	$64._5$	0.5_6	$22._9/87._3$	0.1_4	$5._7/93._1$
9-Fluorenone	103	1.6_8	$68._6$	0.5_1	$20._8/89._4$	0.1_2	$4._9/94._3$
Acenaphthene	101	1.7_2	$70._2$	0.4_8	$19._6/89._8$	0.1_0	$4._1/93._9$
Fluoranthene	101	1.7_0	$69._4$	0.5_0	$20._4/89._8$	0.1_3	$5._3/95._1$
Fluoranthene	103	1.7_6	$71._8$	0.4_7	$19._2/91._0$	0.1_0	$4._1/95._1$
Pyrene	103	1.6_7	$68._2$	0.5_3	$21._6/89._8$	0.1_2	$4._9/94._7$

a) The total amount of anthracene added to the medium was 2.45 μg. b) These values represent relative distances from the beginning of zone-molten ingot. d) The total recovery from the beginning is also shown.

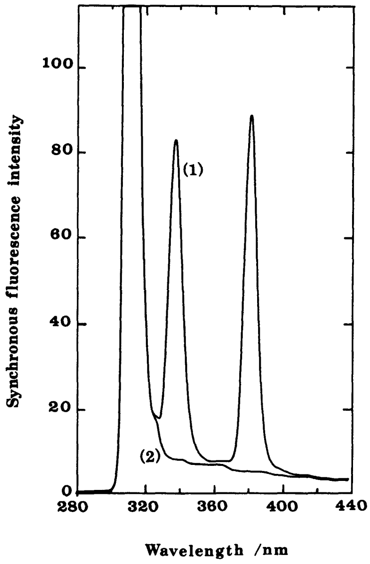

Fig. 3. Synchronous fluorescence spectra of a mixed solution of carbazole, anthracene, and biphenyl and a biphenyl solution.
Wavelength interval (Δλ), 6 nm; solvent, xylene; (1) carbazole (0.2 μg ml^{-1}), anthracene (0.2 μg ml^{-1}), and biphenyl (100 mg ml^{-1}); (2) biphenyl (100 mg ml^{-1}).

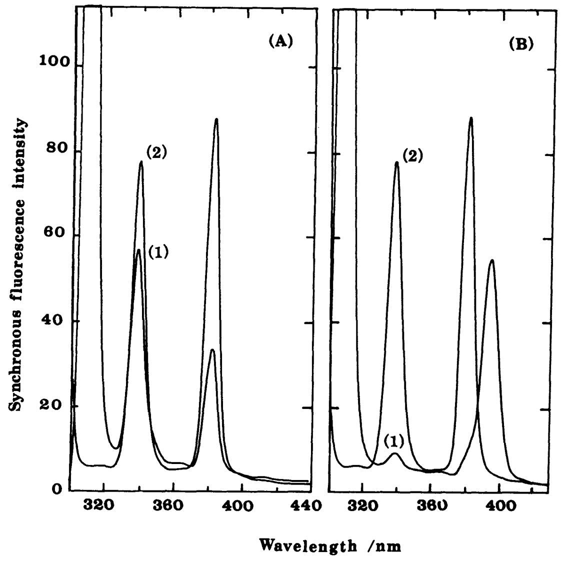

Fig. 4. Synchronous fluorescence spectra of solutions used for the determinations in the practical samples and the standard solution.
Solvent, xylene; Δλ, 6 nm; (A) (1) in the fluoranthene sample; (B) (1) in the chrysene sample; (A) (2) and (B) (2) the standard solution containing both carbazole and anthracene (each 0.200 μg ml^{-1}).

63 to 72% with an average of 67%, 86—91% with that of 88%, and 91—95% with that of 93%, respectively. For the reproducible recovery of anthracene, therefore, it is necessary to use at least the beginning half of the ingot. In the previous dibenzofuran medium, the recovery of anthracene had clearly increased with an increase in the content of other concomitant compounds.[2,3] In this medium, however, such an effect on the recovery could not be definitely observed.

Determinations by Synchronous Fluorescence Spectrometry. Since the simultaneous determination by synchronous fluorimetry has already been reported in the previous papers,[1,5] only the effect of biphenyl on the two analytes was studied. The synchronous fluorescence intensities of carbazole and anthracene gradually increased and decreased, respectively, with an increase in the biphenyl concentration. The variations, however, were so small that the effect of biphenyl could almost be neglected over the wide concentration range from 0 to 180 mg ml^{-1}. Figure 3 (1) represents the spectrum of a ternary solution of biphenyl (100 mg ml^{-1}), carbazole (0.2 μg ml^{-1}), and anthracene (0.2 μg ml^{-1}). The spectrum has three peaks attributable to these three compounds, and their peaks are well-resolved from one another. Consequently, carbazole and anthracene can be successfully determined even in the presence of biphenyl. Calibration curves were prepared by using xylene solutions containing both analytes (0—0.2 μg ml^{-1}), the 0.2-μg ml^{-1} solution being used as the standard. Each of the resulting curves gave a linear relationship between the intensity and the concentration. Both analytes can be determined up to 10 ng ml^{-1} by using the calibration curves.

Application to Practical Samples. The present method was applied to commercially available fluoranthene and chrysene. The zone-molten ingot obtained by treating the fluoranthene sample (100 mg) was cut in two, and the lower half was dissolved in 20 ml of xylene. The solution was further diluted 4 times with xylene. The synchronous fluorescence spectrum of the dilute solution is illustrated in Fig. 4 (A), as well as the standard solution. The spectrum has peaks at 340 and 384 nm, which agree well with those of the standard solution: each analytical value was 106 and 59 ppm, respectively. Next, the spectrum measured for the determination of carbazole in chrysene is shown in Fig. 4 (B). It was obtained by using 20 mg of chrysene as the sample size, cutting the lowest quarter of the zone-molten ingot away, dissolving it in 10 ml of xylene, and diluting the solution 10 times. No anthracene could be determined because the 5*H*-BC contained as a concomitant impurity was inseparable and influential. For the determination of carbazole, however, the interference of 5*H*-BC could be neglected by using a sufficiently dilute solution of the zone-molten sample: the carbazole content was 40 ppm. The above solutions used for these determinations did not show absorption based on interfering impurities at the characteristic wavelengths to be measured. Therefore, the proposed method in the present paper can be applied to such practical samples.

References

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