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C_5-C_{15} hydrocarbons in surface sediments from the Bransfield Strait, Antarctica*

Tang Yunqian (唐运千), Jiang Jiazhen (蒋家桢), Lu Bing (卢冰) and Sui Liangren (眭良仁)
Second Institute of Oceanography, SOA, Hangzhou 310012, China

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Abstract This paper deals with the results of composition of C_5-C_{15} hydrocarbons in the regions of the Bransfield Strait. The multivariate statistical analysis is made to recognize the characteristics of the sediments, resulting in that the C_5-C_{15} hydrocarbons contain n-alkanes, iso-alkanes, cyclo-alkanes, aromatic compounds and their substituted compounds as well. The multivariate statistical analysis also shows that stations G-25 and G-27 have the extreme values of factor after rotation.

Key words C_5-C_{15} hydrocarbons, multivariate statistical analysis, Bransfield Strait.

1 Introduction

The geochemical exploration of oil and gas began in 1930. Due to the imperfect analytical methods, it remained in a low stage over a longer period. From the late sixties, the analytical technique is quickly developing, the application of geochemical exploration has acquired growing interest (Brooks and Kennicutt, 1986; Isaksen, 1991; Plummer, 1992).

In recent years the geochemical exploration has been applicated more and more. There are many methods in exploration of oil and gas, one of them is the absorbent wire (Zhou, 1990). Based on the geochemical analysis it can reflects the situation of underground oil (gas) reservoir.

In the present study, an attempt has been made to study the distributions of n-alkanes, iso-alkanes, cyclo-alkanes and aromatic compounds in surface sediments from the Bransfield Strait, and a comparison has also been made with several samples from the Southern Ocean by the first Chinese investigation. Meanwhile, we tried to use the multivariate statistics methods to assess the potential of oil and gas in the studied area.

2 Sample collection and analysis

The samples of surface sediments were collected during Cruise HY4-901 of the

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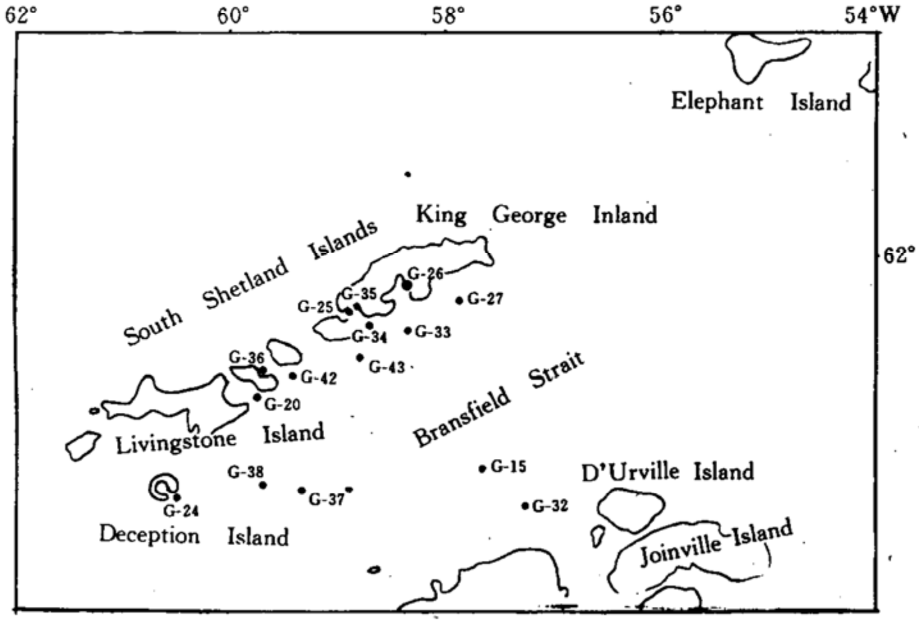

Fig. 1. Sampling stations in the Bransfield Strait.

Ocean IV in October of 1990～March of 1991, by means of a gravity corer. These were offered to us by Guangzhou Marine Geological Survey. The location of sampling station is shown in Fig. 1.

Metallic wire was inserted in sediment, then the absorbed wire sample was heated in Model XP-12 Curie point pyrolysis at 358℃ for 10 s. The pyrolytic product was analyzed by using gas chromatography and gaschromatography-mass spectrometry.

Gas chromatography is performed by GC-9A instrument, which is equipped with a flame ionisation detector (FID), a quartz spring column coated with SE-54. The oven was programmed to 220℃ at 5℃/min with nitrogen as the carrier gas.

Gas chromatography-mass spectrometry was carried out with a Finnigan-MAT 4510 instrument. A quartz spring column (30 m) coated with DB-5. Temperature was programmed to 200℃ at 4℃/min with He as carrier gas. Electron impact was at 70 eV.

3 Result and discussion

3. 1 Characteristics of distribution

Antarctic surface sediments contain C_5-C_{15} hydrocarbons which include n-alkanes, iso-alkanes, cyclo-alkanes, aromatic and their alkyl substituted compounds (Table 1). Sample G25 which located in the valley bottom of island shelf is different from the samples of other stations, it contains the compounds as follows: 1-methyl, 3-ethylbenzene; 1,2,3-trimethylbenzene; 1,3,5-trimethylbenzene; 2-methylnonane; 5-methyldecane

Table 1. Identifiable compounds in sediments

No.	Compounds	No.	Compounds
1	n-pentane	2	2,2-dimethylbutane
3	2-methylpentane	4	3-methylpentane
5	n-hexane	6	methyl-cyclopentane
7	benzene	8	cyclohexane
9	2,3-dimethylpentane	10	2,2,4-trimethylpentane
11	n-heptane	12	methyl-cyclohexane
13	toluene	14	2-methyl-3-ethyl-pentane
15	3,4-dimethyl-hexane	16	3-methyl-heptane
17	1,1-dimethyl-cyclohexane	18	1-methyl, trans-3-ethyl-cyclopentane
19	n-octane	20	iso-propyl-cyclopentane
21	2,2-dimethyl-heptane	22	ethyl-cyclopentane
23	ethylbenzene	24	1,4-xylene
25	4-methyl-octane	26	3-ethyl-heptane
27	1,2-xylene	28	n-nonane
29	iso-propyl-benzene	30	isopropyl-cyclohexane
31	propylbenzene	32	1-methyl-3-ethyl-benzene
33	1,3,5-trimethyl-benzene	34	4-methyl-nonane
35	2-methyl-nonane	36	3-methyl-nonane
37	1,2,4-trimethyl-benzene	38	n-decane
39	1,2,3-trimethyl-benzene	40	1,3-diethyl-benzene
41	5-methyl-decane	42	4-methyl-decane
43	2-methyl-decane	44	3-methyl-decane
45	n-undecane	46	naphthalene
47	n-dodecane	48	n-tridecane
49	n-tetradecane	50	n-pentadecane

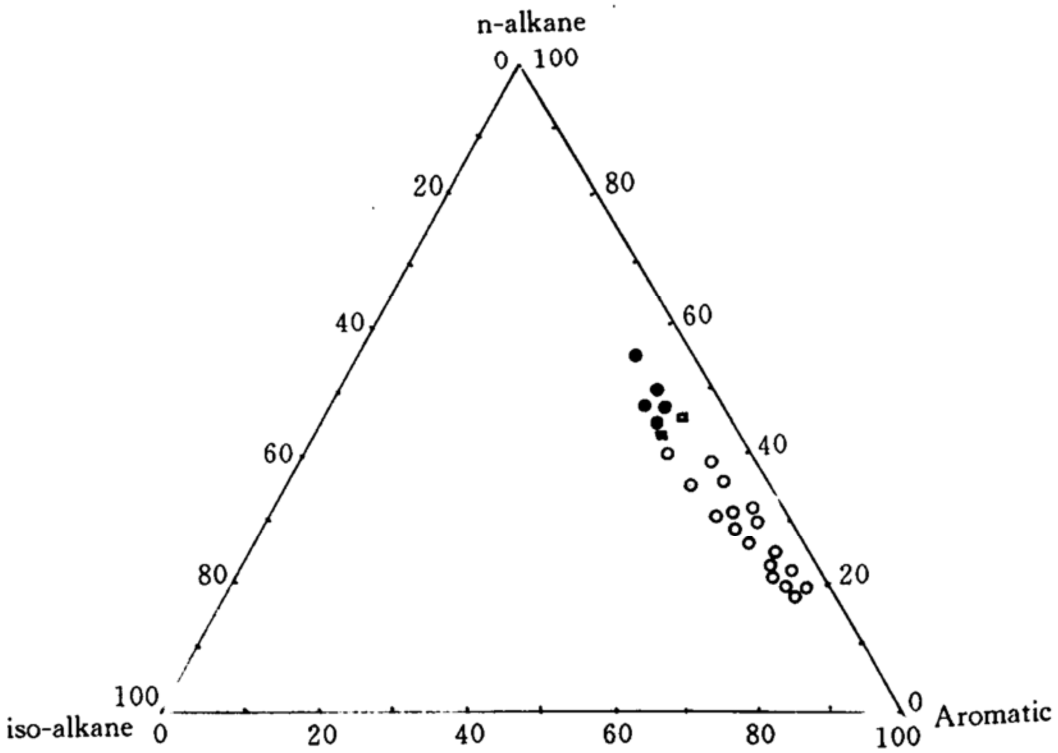

Fig. 2. Triangular diagram of n-alkanes, iso-alkanes and aromatic compounds. ● Cruise 901; ○ First Southern Ocean Samples; □ Zhongshan Station.

and n-propylbenzene compounds, the amounts of these compounds are 0.19%, 0.20%, 0.19%, 0.30%, 0.24% and 0.17% respectively.

During 1984~1985 the surface sediments were first collected by the Chinese scientific investigators in the Southern Ocean which contained some organic compounds. The features of these compounds are: (1) Absence of $C_{13}-C_{15}$ n-alkanes (not including S2 sample with n-dodecane); (2) many isomeric compounds, such as methyl-cyclohexane, 3-methylheptane, ethyl-cyclohexane, 4-methyloctane, 3-methylheptane; isopropyl-cyclohexane and 3-methyldecane; (3) The presence of naphthalene. These features are the same as those of C_1-C_5 hydrocarbons after acid treatment (Lu *et al.* 1996)*.

In Zhongshan Station C-2 and D-6 sediments also have the above compounds, but they are lacking of $C_{12}-C_{15}$ n-alkane compounds. It is interesting that station D-6 contains some special isomeric compounds, such as 2,2-dimethylbutane, 3-methylpentane and 1,1-dimethyl-cyclohexane.

Table 2. Alkane and aromatic compounds

Samples	$\frac{nC_{12}^-}{nC_{13}^+}$	$\frac{nC_{10\text{-}12\text{-}14}}{nC_{11\text{-}13\text{-}15}}$	$\frac{\sum \text{methyl-alkanes}}{\sum \text{n-alkanes}}$	$\frac{\sum \text{dimethyl-alkanes}}{\sum \text{n-alkanes}}$	$\frac{\sum \text{cyclo-alkanes}}{\sum \text{n-alkanes}}$	$\frac{\sum \text{iso-alkanes}}{\sum \text{n-alkanes}}$	Iso-alkanes : cyclo-alkanes : n-alkanes : aromatic
Cruise 901							
G-15	4.12	0.44	0.24	0.00	0.15	0.09	1:1.6:10.9:24.8
G-20	2.78	0.13	0.29	0.02	0.17	0.16	1:1.1:6.4:22.5
G-24	3.28	0.06	0.53	0.01	0.32	0.25	1:1.3:4.0:14.7
G-25	2.25	0.21	0.23	0.01	0.12	0.15	1:0.8:6.5:15.4
G-26	1.13	0.09	0.25	0.01	0.12	0.17	1:0.8:5.8:11.8
G-27	1.44	0.21	0.19	0.01	0.12	0.11	1:1.1:9.6:40.0
G-32	1.68	0.14	0.44	0.01	0.30	0.16	1:1.9:6.4:13.5
G-33	1.48	0.17	0.24	0.00	0.13	0.12	1:1.1:8.5:13.8
G-34	2.16	0.13	0.35	0.00	0.19	0.18	1:1.0:5.5:16.6
G-35	2.85	0.10	0.50	0.02	0.34	0.22	1:1.5:4.6:14.3
G-36	1.15	0.04	0.32	0.02	0.21	0.21	1:1.0:4.9:16.7
G-37	1.86	0.04	0.31	0.00	0.20	0.16	1:1.2:6.3:17.8
G-38	1.82	0.08	0.41	0.02	0.25	0.22	1:1.1:4.6:16.6
G-42	2.48	0.12	0.19	0.00	0.12	0.09	1:1.3:11.0:25.2
G-43	1.69	0.08	0.17	0.00	0.11	0.06	1:2.1:18.1:46.6
First Southern Ocean Samples							
S-2	-	0.17	0.23	0.00	0.06	0.23	1:0.3:4.3:5.0
S-3	-	-	0.17	0.00	0.06	0.22	1:0.3:4.5:9.5
S-5	-	-	0.48	0.00	0.19	0.39	1:0.5:2.6:5.2
S-9	-	-	0.43	0.00	0.11	0.47	1:0.2:2.2:3.6
S-23	-	-	0.18	0.00	0.03	0.25	1:0.3:4.0:5.7
S-26	-	-	0.22	0.00	0.07	0.22	1:0.3:4.5:4.6
L-4	-	-	0.32	0.00	0.17	0.31	1:0.6:3.2:5.9
R-2	-	-	0.18	0.00	0.04	0.02	1:0.2:5.1:5.2
Zhongshan Station							
C-2	-	-	0.17	0.02	0.08	0.20	1:0.4:5.0:6.4
D-6	-	-	0.44	0.35	0.51	0.74	1:0.7:1.4:0.9

• Lu Bing, Tang Yunqian and Sui Liangren (1996): The acid treating hydrocarbons of surface sediments from Antarctica, *Donghai Marine Science*, 12(4), In press (in Chinese).

All the above samples had a great number of aromatic compounds-benzene, toluene, xylene and trimethylbenzene. In particular, the higher content of toluene is 75%～81% of total aromatic compounds in the samples of Cruise 901. Table 2 and Fig. 2 show the distributions of alkane and aromatic compounds. The characteristics of samples of Cruise 901 are: the concentration of aromatic hydrocarbons is higher than that of isomeric compounds, cycloalkanes and n-alkanes hydrocarbon. The ratio of these compounds is low in the first Chinese Southern Ocean samples, on the contrary, the value of aromatic compounds is low in the sediment of D-6 station.

The distribution order of magnitude of crude oil is: n- alkanes > aromatics>isomeric alkanes>cyclo-alkanes. In general, the sediments from Cruise 901 and the first Chinese Southern Ocean are: aromatics>n-alkanes; the difference in them is the value of ratio of iso-alkanes and cyclo-alkanes.

Thompson (1979) thought that the various concentration of aromatic compounds depended on the type of kerogen. The light hydrocarbons are produced from the kerogen of marine sediments, in which the contents of benzene and toluene are low, the ratio of benzene to n-hexane is 0.01～0.32; The relative abundances of benzene and toluene are derived from terrestrial kerogen, the ratio of benzene to n-hexane is 1.33～4.04. The ratios of them are 0.47～1.26 and 2.26～4.32 in Cruise 901 and the first Southern Ocean samples respectively.

The relationship of n-alkanes, iso-alkanes and aromatic compounds is shown in Fig. 2. All these samples are concentrated on the right side. In addition, the difference between Cruise 901 and the first Southern Ocean samples lies in the amounts of benzene

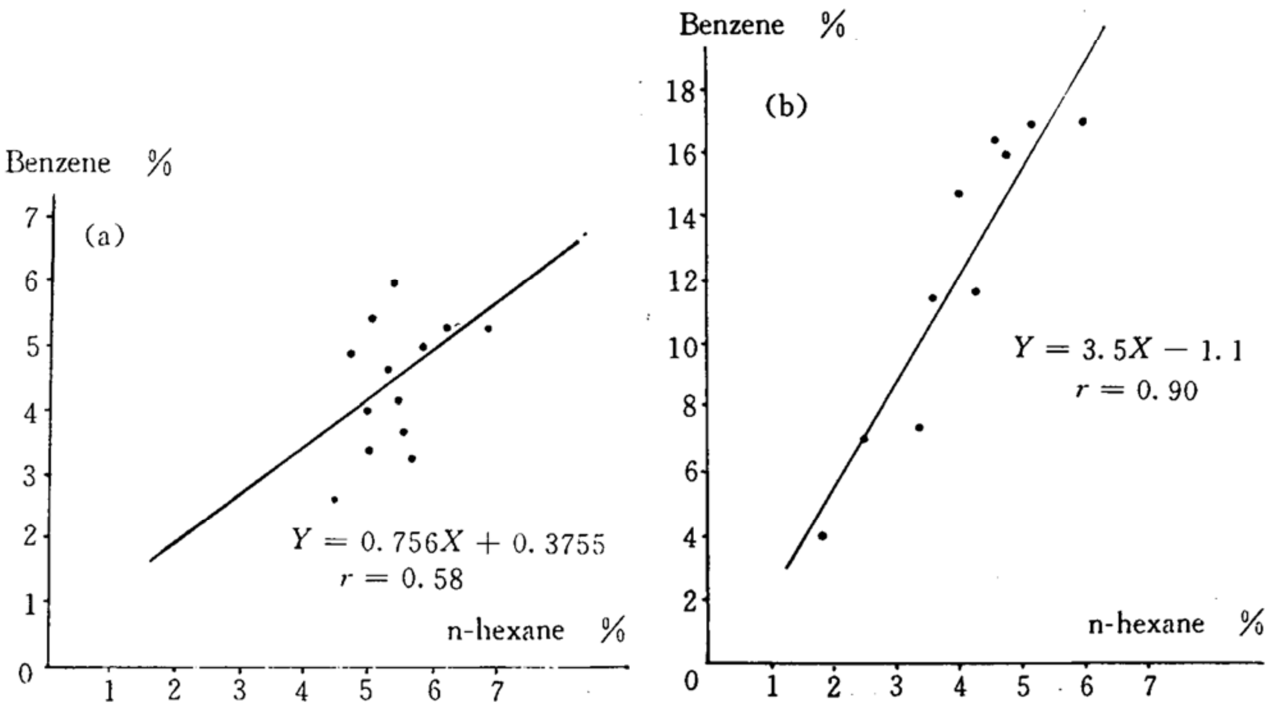

Fig. 3. The relationship of benzene to n-hexane. a: Cruise 901; b: Southern Ocean.

and toluene, in the former they are 3.1%~5.3% and 32.1%~51.5% respectively. But in the latter they are 7.3%~16.8% and 4.1%~12.7% respectively. From Fig. 3 and Fig. 4, we can see that the n-alkanes may be transformed to benzene and toluene through the ring-closing reaction and loss of hydrogen. Several factors can affect the light hydrocarbons (C_1-C_8) distributions, such as bottom currents or slumping, deposition of marine or terrestrial input, generation via either diagenetic or catagenetic process, migration and biodegradation (Whelan, *et al.*, 1988). Hunt *et al.* (1980) carried on microbial degradation of terpenoids in the laboratory and produced those similar to C_1-C_8 compounds in sediments. Thermal generation contain much higher concentration, the product of individual C_1-C_8 alkanes, at least one to three orders of mangitude and much more complex hydrocarbon mixtures (Hunt, 1985). The low concentration of light hydrocarbons present in immature sediments are generally formed from a combination of microbiological and low-temperature chemical process (Whelan *et al.*, 1984).

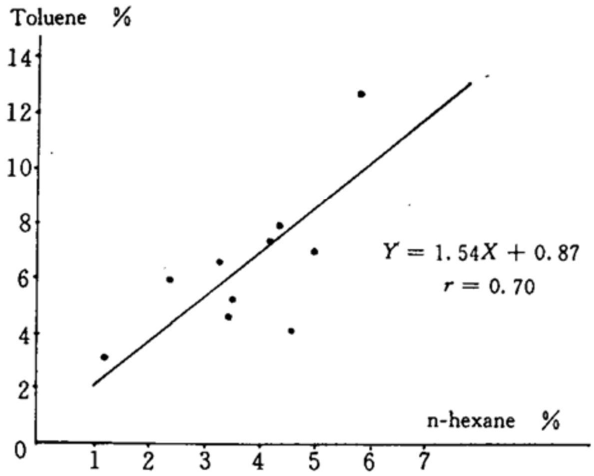

Fig. 4. The relation of toluene to n-hexane (Southern Ocean).

It was mentioned previously that the first Southern Ocean samples were collected in 1984~1985. From Fig. 3 and Fig. 4, it is apparent that the difference exists between the sediments which were collected in different time. During the storage the aromatisation reaction of n-hexane probably occurs in sediments with increasing time and the products tend to be stable. The correlation coefficient of benzene to n-hexane in first Southern Ocean sediments (r=0.90) is greater than that of Cruise 901 samples (r=0.58). It indicates that the time increasing is beneficial to the aromatisation of n-hexanes. It can be seen from Fig. 4 that the relation between n-hexane and toluene also interpretes the effect of time. The correlation coefficient of Cruise 901 is only r=0.01, whereas that of first Southern Ocean samples is r=0.70. The relation between n-heptane and toluene is quite contrary, the Cruise 901 prevailed over the first Southern Ocean sediments (Fig. 5). This proves that there is a possibility of the conversion of n-heptane into toluene. Under the room temperature n-alkanes can partly be aromatized to form stable aromatic compounds.

3.2 Multivariate statistical analysis

In the geochemical studies, the classification of organic matter is made usually by using the coordinate diagram or triangular diagram, the contradiction are present between parameter and sample or between parameters, it is hardly compared to each other. The advantage of multivariate statistical analysis is that the points of sample and variable quantity were reflected in three dimension, two dimension and one dimension spaces from

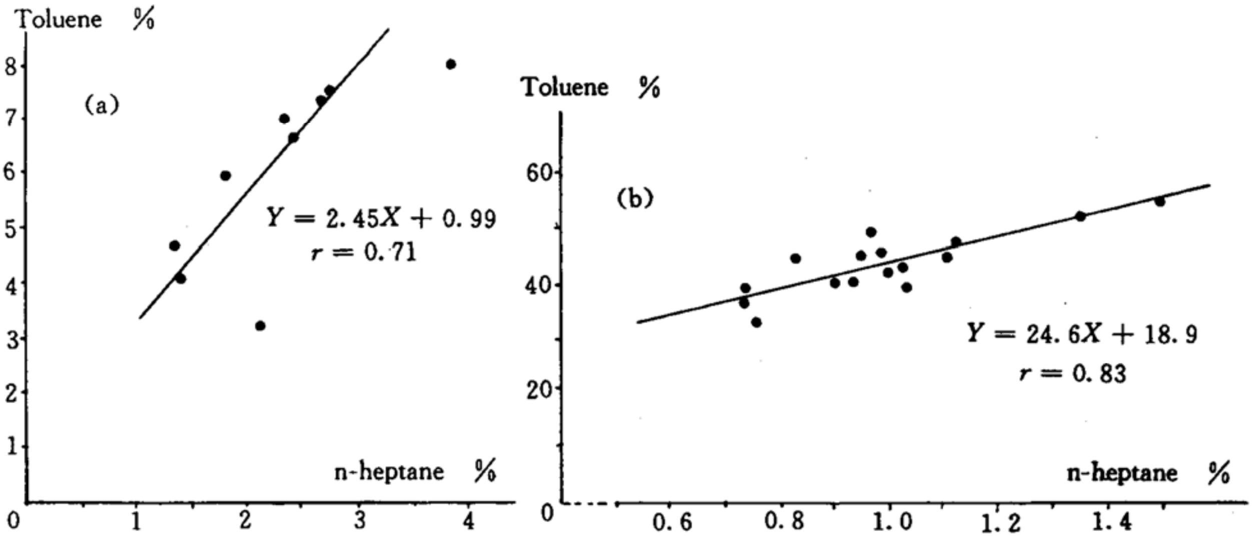

Fig. 5. The relation of toluene to heptane. a: Southern Ocean; b: Cruise 901.

complicated high-dimension space, and so the study of the classification of parameter and sample is made comprehensively and visually (Yu and Li, 1985).

The geochemical parameters are affected by the complex interrelationships between the input source and the similarity in chemical compositions. So in order to know about chemical characteristics of depositional environment, chemical composition of compounds, etc. it requires some simplification of the available data by mathematical treatment. Shaw and Johns (1986) use factor analysis to identify the organic input source of sediment from Santa Catalina Basin. Zumberge (1987) separate the 216 crude oil samples into five different categories, with subsequent simultaneous RQ-mode factor analysis and stepwise discriminate analysis. Mello *et al.* (1988) thought 142 variables to be used as input to principle component analysis of environment class represented by both oil and sources rock samples. Xu (1989)* divide the biomarker compound parameters of different sedimental environment into 4 corresponding analysis. Tang and Liu (1995) explained the source matter and odd-even predominance by using R-type and Q-type factor analysis. To search for a relationship among C_5-C_{15} hydrocarbons composition, the systematic cluster analysis and principle factor analysis were performed. The systematic cluster analysis is the stepwise polymeric classiffcation on the basis of distance and correlation coefficient, we calculated according to the Euclidean distance:

$$d_{i,j} = [\sum_{k=1}^{m}(X_{ik} - X_{jk})^2]^{1/2}$$

Where i, j—i and j samples; $d_{i,j}$—Euclidean distance(between i and j samples); m—

* Xu Jiayou (1989): Data processing of biomarkers and its application to assessment of paleoenvironments. Ph. D. Thesis. Organic Geochemistry Laboratory, Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou (in Chinese)

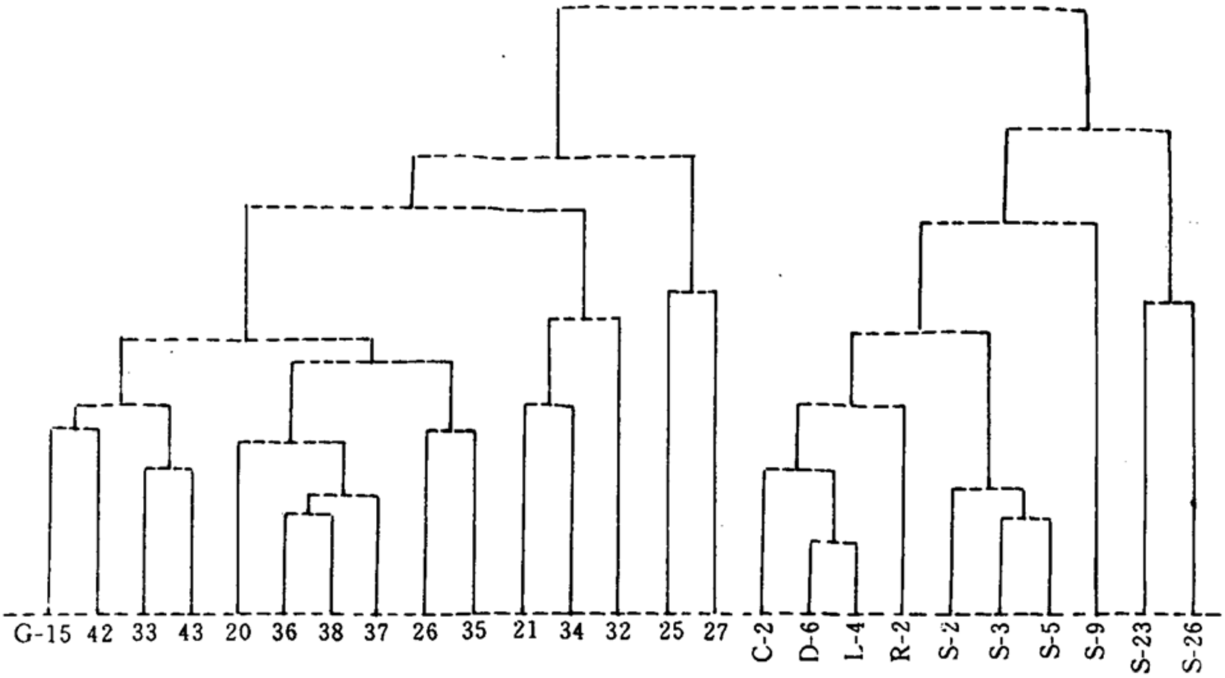

Fig. 6. The cluster analysis of Cruise 901 and the first Southern Ocean sediments.

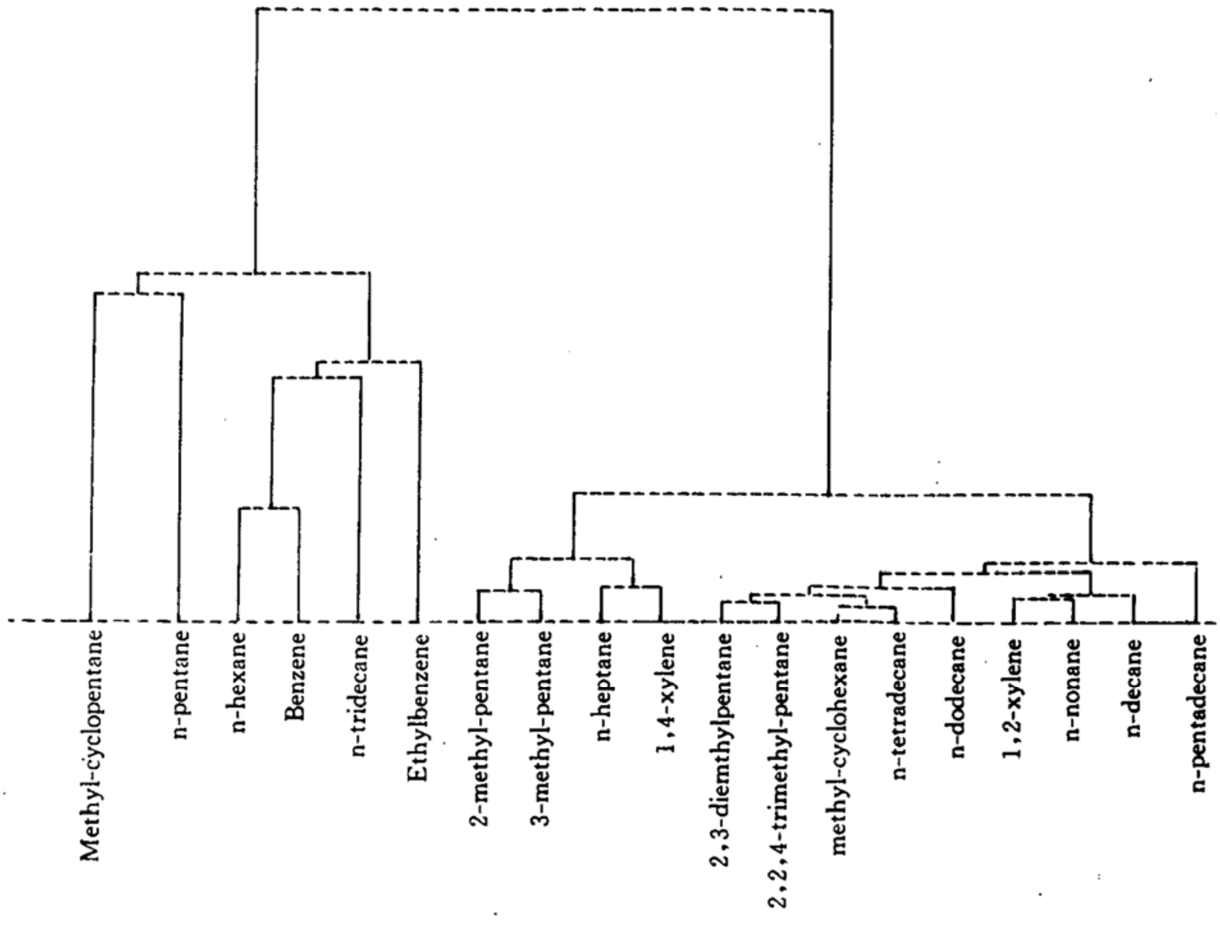

Fig. 7. The composition of C_5-C_{15} hydrocarbons of Cruise 901 samples.

esch sample has m variable quantity(m dimension space); X—value of each variable (analytical data). The clustering category and mergence of samples are done with those of near distance, or the category is done by the correlation coefficient of samples.

We applicate the Q- and R-mode systematic cluster analysis to calculate the twenty-one items data. The maximum distance method of Q-mode reflects the difference between Cruise 901 and the first Southern Ocean sediments, it may be divided into two classes, of them(Fig. 6) G-15 and G-42, G-26 and G-35 had the similar properties, for H/C atomic ratio and O/C atomic ratio of their kerogen lie in the same place in the Van Krevelen diagram(Tang *et al.*, 1995).

Stations C-2 and D-6 and the first Southern Ocean samples all belong to the same category (Fig. 7 and Fig. 8).

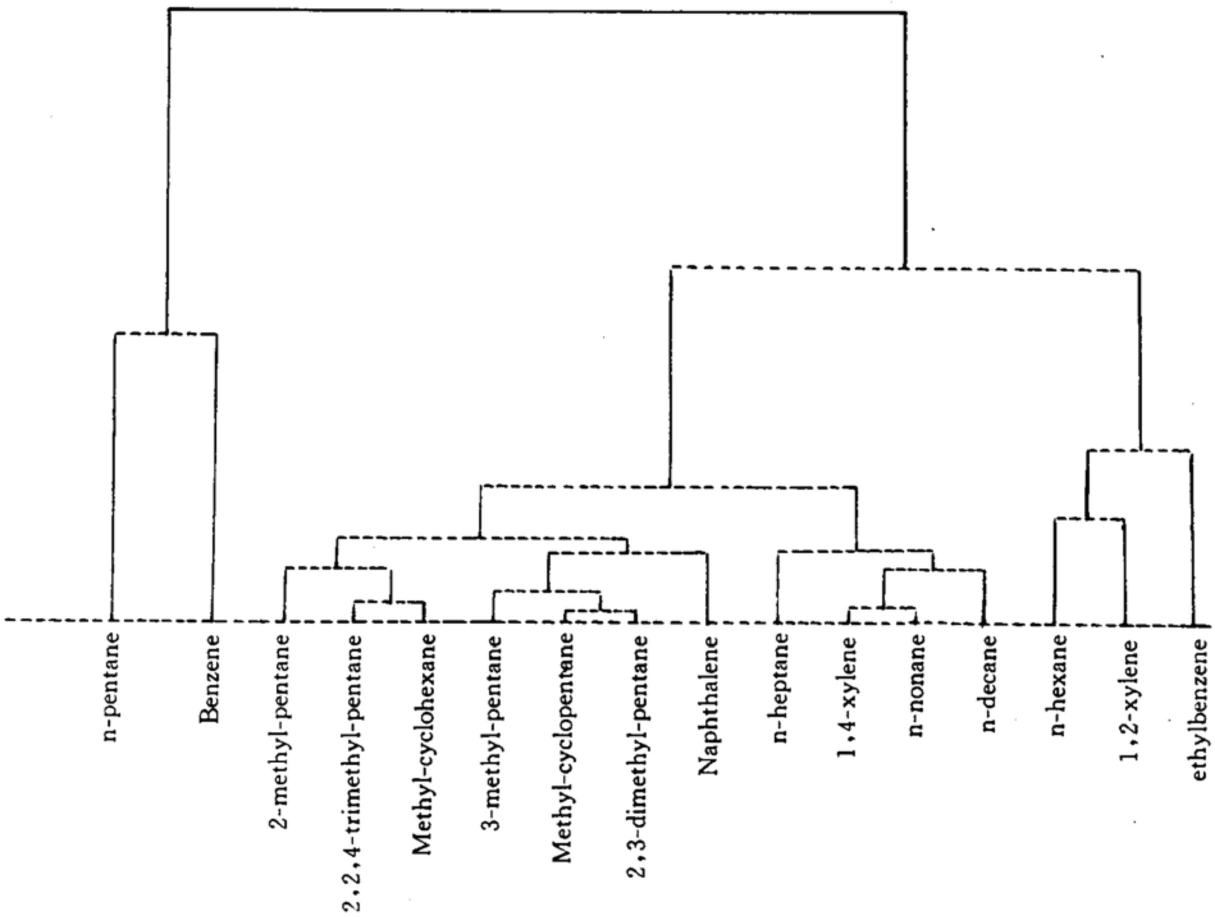

Fig. 8. The composition of C_5—C_{11} hydrocarbons of the first Southern Ocean samples.

Toluene has a higher content, it is removed from the light hydrocarbons, the results are shown by Fig. 8 and Fig. 9. The light hydrocarbons of Cruise 901 and the frist Southern Ocean samples may be divided into two kinds, but they are different in the similarity of individual composition.

Principle factor analysis induced many variables to minor factor, its mathematical model is as follows:

$$Z_i = \sum_{l=1}^{n} a_{il} F_l + e_i , \qquad i=1,2,\cdots,m$$

Where Zi—i number objective (variable); F_l—l number factor; a_{il}—loading of Zi over the F_l; e_i—residual item. Principle factor analysis is made through coordinate rotation in the m dimension (number of variable) space, which needs the maximum variance (the information content is at most). After rotation the coordinate is called factor, factor and original coordinate (variable) have a linear relation, and then find out several maximum variance, i. e. the most factor of information content.

We selected the variance maximum orthogonal rotatory matrix. Orthogonal in each other is a prerequisite for factor loading matrix after rotation. The variance is as large as possible after the square of value. Thus, each value is as large or small as possible, i. e. it splits up towards two termination and data information tends to centrality.

Table 3. Variance maximum orthogonal matrix

Factor/Component	1	2	3
n-pentane	−0. 0115	0. 0463	0. 7557
2-methyl-pentane	0. 4226	−0. 5666	0. 6428
3-methyl-pentane	0. 6380	−0. 1546	0. 4583
n-hexane	0. 7429	−0. 2283	0. 4504
methy1-cyclopentane	0. 2069	−0. 6559	0. 5830
benzene	0. 4069	−0. 3616	0. 6910
2,3-dimethyl-pentane	0. 6854	−0. 0832	0. 0385
2,2,4-trimethyl-pentane	0. 8172	−0. 0635	0. 1064
n-heptane	0. 8355	0. 4423	−0. 0673
methyl-cyclohexane	0. 6180	0. 1964	0. 2872
toluene	0. 8740	0. 2970	0. 1068
ethylbenzene	0. 7529	0. 5250	0. 0276
1,4-xylene	0. 5623	0. 7788	0. 0510
1,2-xylene	0. 4360	0. 8313	0. 0591
n-nonane	0. 0831	0. 7564	−0. 0237
n-decane	−0. 1184	0. 9454	0. 0975
n-dodecane	−0. 0977	0. 4487	0. 6271
n-tridecane	0. 2977	0. 3916	0. 5127
n-tetradecane	0. 3714	0. 2919	0. 6840
n-pentadecane	0. 3798	0. 1271	0. 8214

Table 4. The factor score of sediments after rotation

Factor/ Component	1	2	3	Factor/ Component	1	2	3
G-15	−0. 7092	0. 6523	0. 3424	G-34	0. 2499	−0. 3134	0. 1618
G-20	0. 1418	−0. 1497	−0. 6589	G-35	0. 0223	−0. 4857	0. 1559
G-24	0. 2386	−0. 8127	−0. 3086	G-36	0. 2988	−0. 1172	−0. 5967
G-25	0. 4470	0. 8395	0. 8714	G-37	0. 1227	0. 1219	−0. 3072
G-26	−0. 0226	−0. 0842	0. 1623	G-38	0. 2418	−0. 1376	−0. 3293
G-27	0. 5186	0. 8123	−0. 3387	G-42	−0. 6294	0. 0987	0. 0170
G-32	0. 0645	−0. 4067	0. 8477	G-43	−0. 3721	−0. 1460	−0. 1706
G-33	−0. 6126	0. 1279	0. 1514				

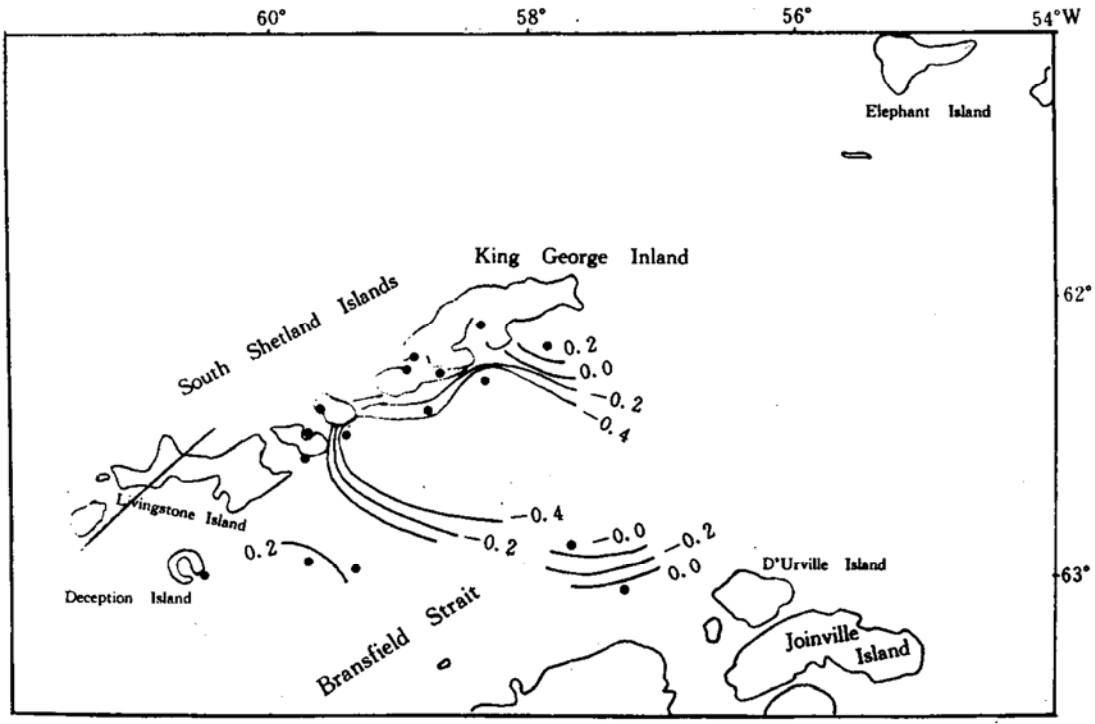

Fig. 9. The contoured diagram of factor 1.

Table 3 shows the variance maximum orthogonal matrix of Cruise 901 samples. It can be seen from the table that three principle factors are important to a part of compositions separately. If the coefficient >0. 6, various composition may be divided into three kinds. These three kinds are others than previous Euclidean distance clusters, due to the difference in the principle of order (cluster, classification). The factor score of Cruise 901 samples after rotation is shown in Table 4. According to the score values, we draw contour diagram respectively as shown in Fig. 9, Fig. 10 and Fig. 11. There were distinct differences among the three contours. It is interesting that in the station G-27 the three factors are all extreme values, the first and second values are positives, the third factor is negative. But in station G-25 the three factors all are positives. Station G-27 is near King Geroge Island Bay and Maxwell Bay, the amounts of planktonic plant are more than 50×10^5 cells/m^3 (Xu and Jian, 1987). Station G-25 is located on the Nelson Bay, the concentration of heterotrophic bacteria are high (>10000 cells/1), and yeast population >50 cells/1 in G-25 sample (Zhang and Sun, 1987). The contents of diatoms are 6000~50000 cells/g in G-25 and G-27 surface sediments (Zhan *et al.*, 1987). In addition, there are many sponge spicules and a few silicoflagellate (Zhan *et al.*, 1987). These indicated that the two stations are different from other stations. Whiticar *et al.* (1985) had collected core samples (length 8. 6 m) from the Basin of King Geroge Island. According to the carbon isotope ratios of methane and ethane, and the vitrinite reflectance, it is suggested that the sediments were in the thermal alteration stage, and probably belonged to condensate accumulation. Based on this situation, it seems necessary to work at some cores near Station G-27 in detail.

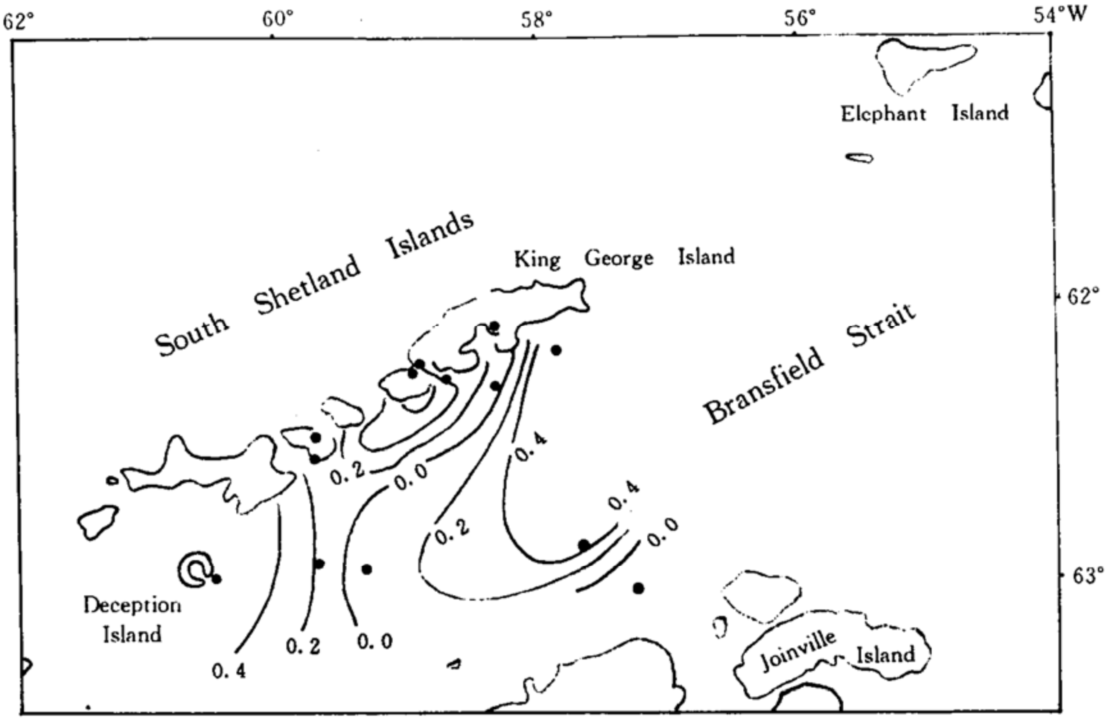

Fig. 10. The contoured diagram of factor 2.

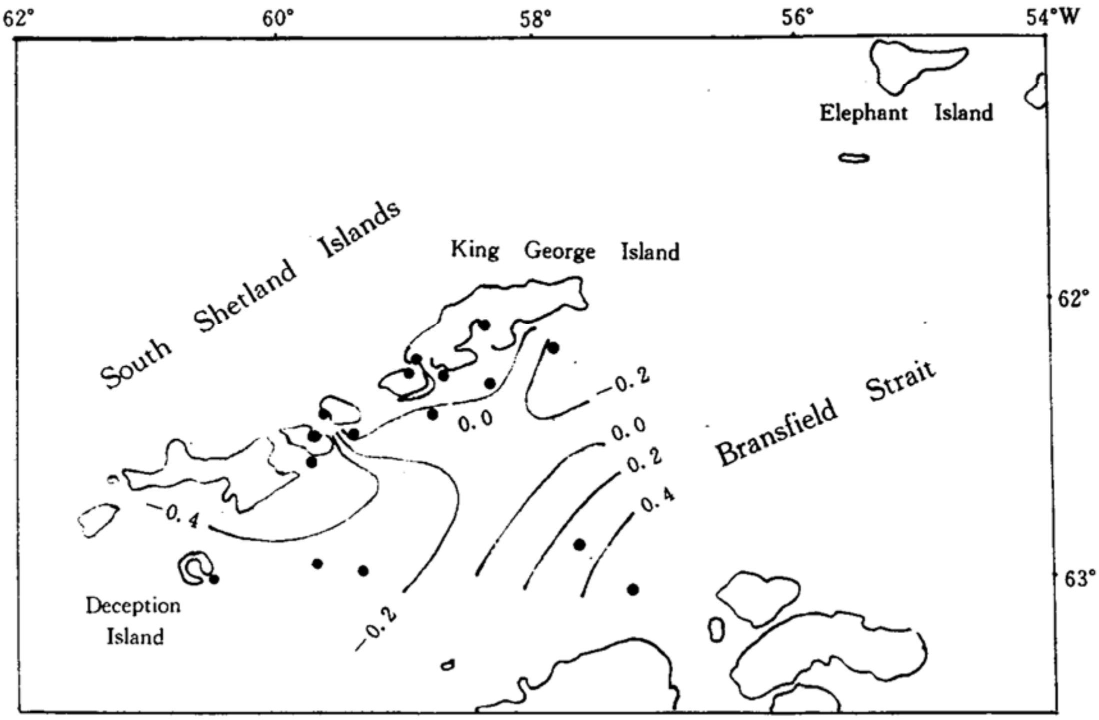

Fig. 11. The contoured diagram of factor 3.

4 Conclusion

(1) Fifty C_5—C_{15} hydrocarbons are present in surface sediments from the Bransfield Strait, these compounds contain n-alkanes, iso-alkanes, cyclo-alkanes and aromatics and their substituted compounds as well.

(2) The results of multivariable statistical analysis indicate that Stations G-25 and G-27 have the extreme values of factor after rotation.

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