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Replacing GB/T 18606-2001

The test method for biomarkers in sediment and crude oil by GC-MS

气相色谱-质谱法测定沉积物和原油中生物标志物

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Foreword

This Standard was drafted in accordance with the provisions of GB/T 1.1-2009.

This Standard is the substitute for GB/T 18606-2001 *The Test Method for Biomarkers in Sediment and Crude Oil by GC-MS*. Compared with GB/T 18606-2001, the major technical changes are as follows:

- The identification of the bicyclic sesquiterpene compound m/z 123 and the illustration of its mass chromatogram were added (SEE 5.4);
- The identification of the naphthalene series compounds m/z 128; 142; 156; 170; 184; 198 and the illustration of their mass chromatograms were added (SEE 5.4);
- The identification of the phenanthrene series compounds m/z 178; 192; 206; 220; 234 and the illustration of their mass chromatograms were added (SEE 5.4);
- The identification of the fluoranthene, perylene and pyrene series compounds m/z 202; 216; 228; 252 and the illustration of their mass chromatograms were added (SEE 5.4);
- The identification of the biphenyl and dibenzofuran series compounds m/z 154; 168; 182 and the illustration of their mass chromatograms were added (SEE 5.4);
- The identification of the dibenzothiophene and benzo-naphthylthiophene series compounds m/z 184; 198; 234 and the illustration of their mass chromatograms were added (SEE 5.4);
- The identification of the fluorene series compounds m/z 166; 180 and the illustration of their mass chromatograms were added (SEE 5.4);
- The quality chromatogram of the original standard was modified (SEE Appendix B).

This Standard was proposed by China National Petroleum Corporation.

This Standard shall be under the jurisdiction of the National Technical Committee for Standardization of Petroleum and Gas (SAC/TC 355).

Drafting organizations of this Standard: Research Institute of Petroleum Exploration & Development, China National Petroleum Corporation; Wuxi Institute of Petroleum Geology, Research Institute of Petroleum Exploration & Development, China National Petroleum Corporation; College of Earth Environment and Water Resources, Yangtze University; Research Institute of

The test method for biomarkers in sediment and crude oil by GC-MS

1 Scope

This Standard specifies the GC-MS identification method and quality requirements for saturated hydrocarbon and aromatic hydrocarbon component biomarkers in sediment and crude oil.

This Standard is applicable to the analysis and identification of biomarker compounds of saturated hydrocarbon and aromatic hydrocarbon components in sediment and crude oil.

2 Normative references

The following documents are essential to the application of this document. For dated references, only the editions with the dates indicated are applicable to this document. For undated references, only the latest editions (including all the amendments) are applicable to this document.

GB/T 6379.1-2004 *Accuracy (trueness and precision) of measurement methods and results - Part 1: General principles and definitions*

3 Methodological principle

The saturated hydrocarbon and aromatic hydrocarbon components prepared from the sediment and crude oil are separated by gas chromatography and detected by mass spectrometry. After being processed by the data processing system, the desired total ion chromatogram, mass chromatogram, and mass spectrum are obtained.

4 Equipment and materials

4.1 Gas chromatography-mass spectrometer: A gas chromatograph with programmed temperature rising function and a mass spectrometer and data processing system with an EI ion source and a maximum scanning mass of not less than 650amu.

4.2 Gas chromatographic column: The stationary phase is 5% benzyl siloxane

5.3.2 Perfluorotributylamine is tuned to the normal operating state. The ratio of each ion peak after tuning should be appropriate. If it is required to comply with spectral library retrieval, the ion peak of m/z 69 shall be tuned to 100%; the ion peak of m/z 219 shall be tuned to less than or equal to 80%, and greater than or equal to 40%; the ion peak of m/z 502 shall be tuned to greater than or equal to 2%, and less than or equal to 5%.

5.3.3 SET the analysis conditions for samples.

5.3.4 After the blank and internal management samples have passed the test, the saturated hydrocarbons and aromatic hydrocarbons are dissolved in n-hexane or dichloromethane prior to sample determination.

5.3.5 CARRY out data processing.

5.4 Analysis report

5.4.1 Mass chromatogram

At least the following spectrograms shall be extracted from the analysis report:

a) Saturated hydrocarbons include:

1) Tricyclic terpane and hopane m/z 191 mass chromatogram, as shown in Figure B.1;
2) Sterane m/z 217 mass chromatogram, as shown in Figure B.2;
3) Bicyclic sesquiterpene m/z 123 mass chromatogram, as shown in Figure B.3.

b) Aromatic hydrocarbons include:

1) Naphthalene series compounds m/z 128; 142; 156; 170; 184; 198 mass chromatograms, as shown in Figure B.4;
2) Phenanthrene series compounds m/z 178; 192; 206; 220; 234 mass chromatograms, as shown in Figure B.5;
3) Fluoranthene, perylene and pyrene series compounds m/z 202; 216; 228; 252 mass chromatograms, as shown in Figure B.6;
4) Biphenyl and dibenzofuran series compounds m/z 154; 168; 182 mass chromatograms, as shown in Figure B.7;
5) Fluorene series compounds m/z 166; 180 mass chromatograms, as shown in Figure B.8.

5.4.2 Qualitative results

SEE Appendix A for the nomenclature of saturated hydrocarbon and aromatic hydrocarbon. For the qualitative results of saturated hydrocarbon, SEE Appendix B for related spectrograms as well as Table 1 (tricyclic terpane and

Table 3 -- Identification table for bicyclic sesquiterpene compounds in m/z 123 mass chromatogram

Peak No.	Molecular formula	Molecular weight	Compound name
1	$C_{14}H_{26}$	194	Bicyclic sesquiterpene (C_{14})
2	$C_{14}H_{26}$	194	Bicyclic sesquiterpene (C_{14})
3	$C_{15}H_{28}$	208	Bicyclic sesquiterpene (C_{15})
4	$C_{15}H_{28}$	208	Bicyclic sesquiterpene (C_{15})
5	$C_{15}H_{28}$	208	8β(H)-drimane (C_{15})
6	$C_{15}H_{28}$	208	Bicyclic sesquiterpene (C_{15})
7	$C_{16}H_{30}$	222	Bicyclic sesquiterpene (C_{16})
8	$C_{16}H_{30}$	222	Bicyclic sesquiterpene (C_{16})
9	$C_{16}H_{30}$	222	Bicyclic sesquiterpene (C_{16})
10	$C_{16}H_{30}$	222	8β(H)-homodrimane (C_{16})

Table 4 -- Identification table for compounds in the mass chromatogram of aromatic hydrocarbons

Peak No.	Mass chromatogram (m/z)	Molecular formula	Molecular weight	Compound name
1	128	$C_{10}H_8$	128	Naphthalene
2	142	$C_{11}H_{10}$	142	2-methylnaphthalene
3	142	$C_{11}H_{10}$	142	1-methylnaphthalene
4	156	$C_{12}H_{12}$	156	2-ethylnaphthalene
5	156	$C_{12}H_{12}$	156	1-ethylnaphthalene
6	156	$C_{12}H_{12}$	156	2, 6-dimethylnaphthalene + 2, 7-dimethylnaphthalene
7	156	$C_{12}H_{12}$	156	1, 3-dimethylnaphthalene + 1, 7-dimethylnaphthalene
8	156	$C_{12}H_{12}$	156	1, 6-dimethylnaphthalene
9	156	$C_{12}H_{12}$	156	1, 4-dimethylnaphthalene + 2, 3-dimethylnaphthalene
10	156	$C_{12}H_{12}$	156	1, 5-dimethylnaphthalene
11	156	$C_{12}H_{12}$	156	1, 2-dimethylnaphthalene
12	170	$C_{13}H_{14}$	170	1, 3, 7-trimethylnaphthalene
13	170	$C_{13}H_{14}$	170	1, 3, 6-trimethylnaphthalene
14	170	$C_{13}H_{14}$	170	1, 3, 5-trimethylnaphthalene + 1, 4, 6-trimethylnaphthalene
15	170	$C_{13}H_{14}$	170	2, 3, 6-trimethylnaphthalene
16	170	$C_{13}H_{14}$	170	1, 2, 7-trimethylnaphthalene + 1, 6, 7-trimethylnaphthalene
17	170	$C_{13}H_{14}$	170	2, 3, 5-trimethylnaphthalene
18	170	$C_{13}H_{14}$	170	1, 2, 4-trimethylnaphthalene
19	170	$C_{13}H_{14}$	170	1, 2, 5-trimethylnaphthalene
20	170	$C_{13}H_{14}$	170	1, 2, 3-trimethylnaphthalene

52	206	$C_{16}H_{14}$	206	2, 3-dimethylphenanthrene
53	206	$C_{16}H_{14}$	206	1, 9 + 4, 9 + 4, 10-dimethylphenanthrene
54	206	$C_{16}H_{14}$	206	1, 8-dimethylphenanthrene
55	206	$C_{16}H_{14}$	206	1, 2-dimethylphenanthrene
56	234	$C_{18}H_{18}$	234	Retene
57	234	$C_{16}H_{10}S$	234	Benzo [b] naphthalene [2, 1-d] thiophenol
58	234	$C_{16}H_{10}S$	234	Benzo [b] naphthalene [1, 2-d] thiophenol
59	234	$C_{16}H_{10}S$	234	Benzo [b] naphthalene [2, 3-d] thiophenol
60	202	$C_{16}H_{10}$	202	Fluoranthene
61	202	$C_{16}H_{10}$	202	Pyrene
62	216	$C_{17}H_{12}$	216	Benzo [a] fluorene
63	216	$C_{17}H_{12}$	216	Benzo [b] fluorene + 4-methylpyrene
64	216	$C_{17}H_{12}$	216	2-methylpyrene
65	216	$C_{17}H_{12}$	216	1-methylpyrene
66	216	$C_{17}H_{12}$	216	Methyl fluoranthene
67	228	$C_{18}H_{12}$	228	Benzo [c] anthracene
68	228	$C_{18}H_{12}$	228	Benzo [a] anthracene
69	228	$C_{18}H_{12}$	228	Chrysene
70	252	$C_{20}H_{12}$	252	Benzo [k] fluoranthene
71	252	$C_{20}H_{12}$	252	Benzo [e] pyrene
72	252	$C_{20}H_{12}$	252	Benzo [a] pyrene
73	252	$C_{20}H_{12}$	252	Perylene
74	154	$C_{12}H_{10}$	154	Biphenyl
75	168	$C_{13}H_{12}$	168	3-methyl biphenyl
76	168	$C_{13}H_{12}$	168	4-methyl biphenyl
77	168	$C_{12}H_8O$	168	Dibenzofuran
78	182	$C_{14}H_{14}$	182	3-ethyl biphenyl
79	182	$C_{14}H_{14}$	182	3, 5-dimethylbenzidine
80	182	$C_{14}H_{14}$	182	3, 3’-dimethylbenzidine
81	182	$C_{14}H_{14}$	182	4-ethyl biphenyl
82	182	$C_{14}H_{14}$	182	3, 4’-dimethylbenzidine
83	182	$C_{14}H_{14}$	182	4, 4’-dimethylbenzidine
84	182	$C_{13}H_{10}O$	182	Methyl dibenzofuran
85	182	$C_{13}H_{10}O$	182	Methyl dibenzofuran
86	182	$C_{13}H_{10}O$	182	Methyl dibenzofuran
87	166	$C_{13}H_{10}$	166	Fluorene
88	180	$C_{14}H_{12}$	180	2-Methyl fluorene
89	180	$C_{14}H_{12}$	180	1-Methyl fluorene

3) Steranes shall be named for configurations at carbon positions 5, 8, 9, 10, 13, 14, 17, and 20. However, since some of these configurations are stable and some cannot be changed by hydrogen exchange, regular sterane only needs to be labeled as the configurations at carbon positions 5, 14, 17 and 20, and diasterane only needs to be labeled as the configurations at carbon positions 13, 17 and 20.
4) The nomenclature of hopane only needs to indicate the configurations at carbon positions 17, 21, and 22.
5) Carbon loss and carbon addition: “nor-” for carbon loss, “homo-” for carbon addition, and “nor-” or “homo-” group rankings are indicated by Arabic numerals. For instance, 17α(H)-22, 29, 30 trisnorhopane; 17α(H), 21β(H)-30 homohopane (22R). In case of ring carbon loss or carbon addition, English capital letters A, B, C … shall be added before “nor-” or “hemo-” to mark the indicated ring. For instance, 5α(H)-A-norcholestane.
6) Ring opening: Steroid and terpene rings are separated by “(seco-)”, and the position of broken bonds is indicated by Arabic numerals. For instance, 8, 14-seco-hopane.
7) In hopane, the methyl group shifts from C-18 to C-17. The methyl group at the C-18 position is replaced by H, which is denoted by “neo-”. For instance, 18α(H)-30 norneohopane (C_{29}Ts).

d) Abbreviation

In order to facilitate geological applications, steranes and terpanes can be used as abbreviations commonly used at home and abroad. The principle is to omit the Arabic numerals for the chiral carbon position of the ring and the hydrogen, and to name them according to the number of carbon atoms contained, as shown in Table A.1.

Table A.1 -- Abbreviations of sterane and terpane compounds

Chemical nomenclature	Abbreviation
5α(H), 14α(H), 17α(H)-C_{27} sterane (20R)	ααα-C_{27} sterane (20R)
24-methyl-5α(H), 14β(H), 17β(H)-C_{28} sterane (20S)	αββ-C_{28} sterane (20S)
24-ethyl-5α(H), 14α(H), 17α(H)-C_{29} sterane (20R)	ααα-C_{29} sterane (20R)
4-methyl, 24-ethyl-5α(H), 14α(H), 17α(H)-C_{30} sterane (20R)	ααα-C_{30} 4-methyl sterane (20R)
17α(H)-C_{27} trisnorhopane	Tm
17β(H), 21α(H)-C_{29} hopane (normoretane)	βα-C_{29} normoretane
17α(H), 21β(H)-C_{30} hopane	αβ-C_{30} hopane
17α(H), 21β(H)-C_{31} hopane (22R)	αβ-C_{31} hopane (22R)

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