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Core Structure Analysis of Heavy Oil Components with Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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In this study, a core structure estimation method for molecules in heavy petroleum fractions was developed based on Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). The mass analysis of molecules in Middle Eastern vacuum residue was performed by a combination of FT-ICR MS with a fractionation technique. In addition, to obtain mass information about the core structures, collision induced dissociation Fourier transform ion cyclotron resonance mass spectrometry (CID FT-ICR MS) was performed for the three or more-ring aromatic fraction (3A ♫) and asphaltene (As) fractions. The differences in the double bond equivalent (DBE) distribution before and after CID indicate that the dissociation of the internal linkages of the parent ions had occurred, implying that archipelago-type molecules were contained in the 3A ♫ and As fractions. The proposed method enabled us to assign a core structure to each detected fragment ion successfully. The estimated core structures of the As fraction are similar to the core structures proposed in previous studies. Thus, the proposed method provides reasonable core structures for heavy petroleum fractions.

Keywords
FT-ICR MS, Collision induced dissociation, Heavy oil, Core structure estimation

1. Introduction

Technological development and improvement in heavy oil upgrading technologies are required to utilize heavy petroleum feedstock efficiently in refineries because the produced crude oil is heavy and inferior. It is essential to understand the reactivities and physical properties of feedstocks in process development. Regarding atmospheric distillates, such as naphtha, kerosene, and diesel, component data have been obtained through conventional analyses, e.g., gas chromatography-mass spectrometry (GC-MS) 1), GC-field ionization mass spectrometry (GC-FIMS) 2), and two-dimensional GC (2DGC) 3),4). High temperature 2DGC 5) and a combination of multidimensional liquid chromatographic separation and high-resolution mass spectrometry 6),7) has been used for the characterization of vacuum gas oil. However, it is challenging to use these techniques with heavy petroleum feedstocks because they are complex mixtures with many components and these components have significant structural and chemical variety. If conventional gas chromatographic analysis methods are applied for heavy petroleum fractions, the analysis temperature must be increased, often exceeding the decomposition temperature because the heavy petroleum fraction contains compounds that have a high boiling point. Therefore, these methodologies are not sufficient to analyze the nature of heavy petroleum fractions without decomposition.

Compositional and structural data of heavy oil components are fundamental for understanding the characteristics of the heavy petroleum feedstocks. In particular, the core structure, which is composed of aromatic rings, naphthenic rings, and heteroatom-containing functional groups, is the most important structure because of its effects on reactivity and physical properties. In the last decade, analytical techniques have advanced significantly, for example, high-resolution mass spectrometry, and this has made it possible to obtain molecule-level information about heavy petroleum feedstocks. In particular, the combination of Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) and soft ionization techniques, such as atmospheric pressure photoionization (APPI), is an excellent tool to obtain structural and compositional information about highly complex mixtures of hydrocarbons 8).
components in heavy petroleum fractions are aromatic compounds with or without heteroatoms\(^9\). APPI can be used for the ionization of aromatic compounds\(^10\). Therefore, APPI FT-ICR MS analysis enables the major component analysis of heavy petroleum feedstocks. The molecular structures of the component compounds have been analyzed by coupling ultrahigh-resolution mass spectrometry with a fragmentation method. Podgorski et al. characterized deasphalted oil and its fractions using a combination of APPI FT-ICR MS analysis and infrared multiphoton dissociation (IRMPD)\(^11\). This analysis revealed that both island and archipelago-type molecules were present in each aromatic ring fractions. Qian et al. determined the typical aromatic building blocks contained in heavy petroleum fractions by FT-ICR MS with collision induced dissociation (CID)\(^12\). Their studies provided basic knowledge about the fragmentation of both island and archipelago-type molecules in CID analysis, indicating that the vacuum residue (VR) contains both island and archipelago-type structures.

Computational modeling technologies have also promoted the understanding of the nature of heavy petroleum fractions. Zhang et al. proposed the stochastic method for the determination of the structures and compositions of molecules in heavy petroleum feedstocks\(^13\). The building block library contained above 600 blocks, constructed based on the extrapolation of the chemical characteristics of light hydrocarbons and the precise mass measurements of heavy oil fragmentation products. The abundance of each molecule was quantitatively determined by adjusting the probability density functions (PDFs) of each structural attribute based on several analytical data, such as the density, elemental composition, and molecular weight. These structural and compositional data agreed well with the analytical data obtained by FT-ICR MS analysis.

Although these analytical and computational advances have provided a better understanding of the structure and composition of heavy petroleum fractions, there is no methodology to propose the structure of whole components in heavy petroleum fractions based on FT-ICR MS analysis. Comprehensive structural information about heavy petroleum feedstocks will increase the understanding of the reactivity and properties of heavy hydrocarbon compounds and will accelerate the development of heavy oil upgrading technology.

In this study, an estimation method for the core structures comprising heavy petroleum fractions is proposed. Cho et al. reported that prefractionation, such as saturates, aromatics, resins, and asphaltenes (SARA) fractionation, is required to improve the ionization efficiency in FT-ICR MS analysis because of the matrix effects of other components\(^14\). In this study, a modified SARA fractionation method\(^15\) was applied before the FT-ICR MS analysis of the heavy oil sample. A list of possible core structures in the heavy petroleum feedstock was constructed based on the carbon number and double bond equivalent (DBE) distributions obtained by FT-ICR MS analysis. The mass data of core structures was obtained by CID analysis and the core structure assignment was performed by comparing the CID mass data to the mass data of the core structure list. The applicability of this method for the core structure estimation of heavy petroleum samples is discussed.

2. Experimental

2.1 Pre-treatment of Samples

Middle Eastern VR was used as a sample in this study. Before FT-ICR MS analysis, this sample was separated into some sub-fractions by a modified SARA fractionation method\(^15\). The procedures for sample separation are shown in Fig. 1. First, 2.6 g of Middle Eastern VR was dissolved in 60 mL of n-heptane. This solution was stirred and heated to reflux for 1 h, then, it was cooled to room temperature. The heptane-insoluble solid was collected by suction filtration with Japan Industrial Standard (JIS)-grade 5C filter paper. The heptane-insoluble solid was extracted by Soxhlet extraction with 150 mL of toluene for 6 h. After the extraction, the toluene solution was rotary evaporated and dried in a vacuum oven at 110 °C for 1 h. This toluene solution was collected as the asphaltene fraction (As). The n-heptane solution (as the maltene fraction) was also rotary evaporated and dried, as for the toluene-soluble solution. Subsequently, the dried maltene fraction was separated into six fractions (the satu-rate fraction (Sa), one-ring aromatic fraction (1A), two-ring aromatic fraction (2A), three or more-ring aromatic fraction (3A+), polar resin fraction (Po), and polyaromatic resin fraction (PA)) by column chromatography. A glass column packed with activated neutral alumina gel on activated silica gel was used. In the column, 50 g of alumina gel and 40 g of silica gel were baked for 15 h at 400 °C and 250 °C, respectively, before use. Then, 1.5 g of the dried maltene fraction was redissolved in 40 mL of n-heptane and n-heptane solution was introduced into the column to adsorb the maltene fraction onto the surface of the silica bed. In sequence, 210 mL of n-heptane, 250 mL of n-heptane/toluene mixture (95/5, v/v), n-heptane/toluene mixture (90/10, v/v), 250 mL of toluene and 250 mL of ethanol were used to elute Sa, 1A, 2A, 3A+, and Po. Finally, elution using 100 mL of chloroform and 100 mL of ethanol was carried out twice to collect the PA. The yield of each fraction is shown in Table 1.

2.2 FT-ICR MS Analysis

Analyses were performed with a 12 T FT-ICR MS (solariX 12T, Bruker Japan K. K.). Several kinds of ionization methods have been proposed for the analysis of petroleum samples. However, the suitable ioniza-
The sample method for the analysis depends on the characteristics of sample and it is required to select the suitable method considering their features. In this study, three kinds of ionization methods were selected and used them for a single petroleum sample: APPI, laser desorption ionization (LDI), and laser desorption combined with silver cationization (LDI-Ag) [16]. The 1A, 2A, 3A, and Po fractions were analyzed with APPI, whereas LDI and LDI-Ag were used for the analyses of As and Sa, respectively. The major components of the PA and As fractions are polyaromatic hydrocarbons (PAHs), whereas those of Sa fraction are saturated cyclic and non-cyclic hydrocarbons, such as naphthenic compounds and paraffins. Highly condensed PAHs have high boiling points. Therefore, it is difficult to detect these compounds efficiently by APPI because of their low vaporization efficiency. On the other hand, saturated hydrocarbons were not detected sufficiently because saturated hydrocarbons have an ionization potential higher than the photon energy used in APPI [17]. LDI-Ag can improve the ionization efficiency of saturated molecules and makes it possible to analyze the characteristics of these molecules.

The samples containing 1A, 2A, 3A+, and Po fractions were dissolved in high-performance liquid chromatography (HPLC) grade toluene (Wako Pure Chemical Industries, Ltd.) at 0.5 mg/mL. These solutions were diluted 2 to 4 times with toluene before analysis. The PA and As fraction samples were dissolved in HPLC-grade chloroform (Wako Pure Chemical Industries, Ltd.) at 50 mg/mL. Then, 1 mg of this solution was pipetted onto a target plate (MTP 384 ground steel BC target plate, Bruker Japan K. K.), and this target plate was dried to remove solvent before analysis. Regarding the Sa fraction, a sample was prepared in accordance with the procedures reported previously [16]. All analyses were performed in positive ion mode.

In addition to the mass measurement of molecules in each fraction, fragmentation and fragment ion mass analysis were performed to measure the mass of structural building blocks. CID was used for the fragmentation of the parent ions. The difference in molecular structures between island-type molecules and archipelago-type molecules is shown in Fig. 2. These molecules have three structural attributes: the core, side chains, and internal linkages. It has been reported that there are two types of molecule in heavy petroleum fractions: island-type (single-core) molecules [18,19] and archipelago-type (multi-core) molecules [20]. The C-C single bonds in the C2+ side chains and internal linkages can be dissociated by CID, and the fragment ions of the core are generated. Mass information about the core structure can be obtained by FT-ICR MS analysis combined with CID fragmentation (CID FT-ICR MS).

The spectrum analysis software Composer (Sierra Analytics, Inc.) was used for the primary analysis of the spectra obtained by FT-ICR MS analysis, yielding the mass calibration and molecular formula. An original analysis tool, the so-called Composition and Structure

Table 1 Yield of Each Fraction in Sample Fractionation

| Fraction                | Yield [wt%] |
|-------------------------|-------------|
| Saturate (Sa)           | 15.1        |
| 1-ring aromatic (1A)    | 11.2        |
| 2-ring aromatic (2A)    | 7.5         |
| 3+ -ring aromatic (3A+) | 32.5        |
| Polar resin (Po)        | 11.1        |
| Polyaromatic resin (PA) | 15.5        |
| Asphalten (As)          | 6.5         |
| Toluene insoluble       | -           |
| Loss                    | 0.5         |
| Total                   | 100.0       |

Fig. 1 Procedures for Sample Separation

![Fig. 1 Procedures for Sample Separation](image-url)
Analysis Tool (CSA), was built in MATLAB (MathWorks, Inc.). This tool was used for the visualization of the FT-ICR MS analysis and core structure estimation.

3. Results and Discussions

3.1. Hetero Cass Distributions

Mass spectra of the 3A+ and As fractions obtained by FT-ICR MS analysis are shown in Fig. 3. The mass-to-charge (m/z) ratios of the 3A+ and As fractions ranged between 300 and 1000. However, the modes of m/z distribution, which were m/z values had the highest intensity of all detected peaks in the sample, were around 600 for the 3A+ fraction and 400 for the As fraction. The Sa, 1A, 2A and Po fractions were distributed at the almost same range of the 3A+ fraction. In contrast, the PA fraction had a similar distribution to the As fraction. The As fraction had a narrower m/z distribution than that of the 3A+ fraction. This difference is due to the differences in the ionization method. It has been reported that APPI provides a broader distribution that extends to higher masses, whereas LDI produces distributions that show lower molecular weight peaks\(^2\)\(^1\),\(^2\)\(^2\). The trends observed by us agree with these reports.

The assigned molecules were classified into each hetero atom class based on their molecular formulas. In total, 21 heteroatom classes were measured in this analysis. The abundances of five major heteroatom classes (HC (no heteroatoms), S1 (one sulfur atom), S2 (two sulfur atoms), N1 (one nitrogen atom), and N1S1 (one nitrogen and one sulfur atom)) are compared in Fig. 4 for each fraction. The relative abundance was calculated using Eq. (1).

\[
\text{Relative abundance [%]} = \frac{\sum I_{ij}}{\sum \sum I_{ij}} \times 100 \quad (1)
\]

Here, \(I\) is the intensity observed in the FT-ICR MS analysis, and \(i\) and \(j\) are the hetero class and the number of peaks, respectively. Over 90% of the molecules in the Sa fraction were classified in the HC class, mostly paraffins. The 1A, 2A, and 3A+ fractions are mainly composed of sulfur compounds, classified as S1 and S2, and the abundance of S2 class molecules increased as the number of aromatic rings increased. On the other hand, the Po, PA, and As fractions contained many nitrogen compounds classified in N1 and N1S1 classes. The reason why these classes have a high relative abundance is because LDI is very sensitive to aromatic nitrogen-containing compounds, as reported in previously\(^2\)\(^2\).

Regarding the Po fraction, the total abundance of these five classes was 41.6%, although it was higher than 80% in other fractions except for the Po fraction. The most kinds of heteroatom classes, 15 classes, were observed in the Po fraction. The abundance of oxygen-
containing molecules, such as the O1S1 (15.1 %), O1S2 (10.2 %), and N1O1 (8.8 %) classes, were particularly high, except for the five major classes. This indicates that the molecules in the Po fraction contained various functional groups with heteroatoms. In addition, it was estimated that the molecules in the Po fraction had a greater polarity than those of the molecules of other fractions because the abundance of nitrogen and oxygen-containing classes was higher. In this study, the Po fraction was eluted with a polar solvent (ethanol) in the column chromatography. Therefore, polar compounds contained in the VR sample were mainly collected in the Po fraction. These class distributions are consistent with the characteristics of Po fractions.

3. 2. Carbon Number and DBE Distributions

The DBE and the carbon number (C#) distributions were compared for all fractions. The DBE and C# distributions of the HC, S1, and N1 classes are shown in Fig. 5. For an elemental formula of C\(_c\)H\(_h\)N\(_n\)O\(_o\)S\(_s\), the DBE was calculated from Eq. (2)\(^{23}\):

\[
DBE = c - \frac{h}{2} + \frac{n}{2} + 1
\]

(2)

The DBE represents the number of rings plus double

Dashed line indicates the planar aromatic limit.

Fig. 5 DBE and Carbon Number Distributions of HC, S1, and N1 for Each Fraction
bonds to carbon. For example, the DBE value of benzene (one-ring aromatic), naphthalene (two-ring aromatic), and anthracene (three-ring aromatic) are 4, 7, and 10, respectively. For Sa, 1A, 2A, and 3A, the DBEs are $0 < \text{DBE} < 5$, $5 < \text{DBE} < 10$, $10 < \text{DBE} < 15$, and $15 < \text{DBE} < 20$, respectively. These fractions were separated by aromaticity. These results, thus, show the characteristics of these fractions. The Po fraction is distributed in the same DBE-C# area as the 3A+ fraction. This indicates that Po fraction has same aromaticity as the 3A+ fraction, but their polarities are different, as shown in the heteroatom class distribution. The PA and As fractions had higher DBE values than those of the other fractions: $15 < \text{DBE} < 25$ for the PA fraction and $20 < \text{DBE} < 30$ for the As fraction. In addition, the C# distribution of the As fraction was $20 < \text{C#} < 50$, narrower than that of the other fractions ($25 < \text{C#} < 70$). Regarding the C# distribution in the HC class, the Po fraction had the narrowest distribution, however, the abundance of this class was 0.8% in the Po fraction and the As fraction had the narrowest C# distribution in the HC, S1 and N1 classes when focusing on the major hetero classes. The dashed lines in Fig. 5 show the planar aromatic limit, which is the upper DBE boundary value for C# hydrocarbons\textsuperscript{24,25}. The molecules in the As fraction are populated along this line. This indicates that the molecules contained in the As fraction were highly condensed, and they had short alkyl side chains.

### 3.3. CID FT-ICR MS Analysis

CID FT-ICR MS analysis was performed for all fractions to measure the mass of core structures. The DBE and C# distributions of the 3A+ and As fractions before and after CID are shown in Fig. 6. The 3A+ fraction has a broad distribution in DBE and C# before CID. However, the C# distribution range was narrower and moved to a smaller C# range after CID because of the dealkylation of molecules. The C# distribution of the As fraction also shifted to smaller C#. In addition, the DBE distribution of the As fraction moved drastically to a lower DBE. To confirm the change in the DBE distributions, the DBE distribution of the As fraction is shown in Fig. 7. The 3A+ fraction ranged from 4 to 26 in DBE before CID. DBEs of 4 and 26 are equivalent to one-ring and 9-10-ring aromatics. After CID, the DBE distribution moved to 2-19. DBEs of 2 and 19 are equivalent to two-ring naphthenic and 6-7-ring aromatics. Regarding the As fraction, the DBE distributions were different between before and after CID as well. The As fraction ranged from 10 to 38 in DBE before CID. DBEs of 10 and 38 are equivalent to three-ring and 13-15-ring aromatics. After CID, the DBE distribution moved to 5-25. DBEs of 5 and 25 are equivalent to one-ring aromatic with one naphthene ring (such as tetralin) and 8-10-ring aromatics. The difference of the DBE distributions between before and after CID in the As fraction was larger than that of the 3A+ fraction. It implied that the As fraction con-
tained more archipelago-type molecules than the 3A fraction. In addition, DBEs of the As fraction after CID was larger than that of the 3A fraction. It indicated that the As fraction was composed of molecules which had higher condensed aromatic cores than the 3A fraction. This change in the DBE distribution was due to the dissociation of internal linkage in multicore molecules. This result implied that multicore molecules are present in the As fraction. On the basis of the CID FT-ICR MS analysis, the core structures in the molecules were estimated, as reported in the following section.

3.4. Core Structure Estimation

In this study, core structures included in each fraction by comparing the mass obtained in CID FT-ICR MS analysis with the mass of the possible core structure. To assign the core structure for the mass spectrum obtained in CID FT-ICR MS analysis as much as possible, possible core structures were built as comprehensively as possible and the list of core structures was prepared prior to the core structure assignment. Core structure estimation was performed by the following three steps: (1) Construction of basic core structure list; (2) core structure building; and (3) assignment of the core structure based on the mass data obtained from CID FT-ICR MS. First, the list of basic core structures was constructed. The basic core structures were defined as the core consisting of aromatic rings and peri-condensed naphthenic rings. Examples of the basic core structures built in this study are shown in Fig. 8. The maximum aromatic ring number contained in a single core was eight. The maximum DBE obtained in CID FT-ICR MS analysis was 26 and it was equivalent to 8-10-ring aromatics. However, cores are composed of not only aromatic rings but also naphthenic rings and/or heteroatom rings and they also increase the DBE of cores. Therefore, the lower aromatic ring numbers expected from the maximum DBE was defined as the maximum allowable ring number in this study. In building basic core structures, both peri-condensed and cata-condensed structure were considered.

Secondly, core structures used for assignment were built. An outline of the procedures in this step is shown in Fig. 9. In this step, cata-condensed naphthenic

![Fig. 7 Comparison of the DBE Distributions of the 3A+ and As Fractions before and after CID](image)

![Fig. 8 Example of Core Structures Listed in the Basic Core Structure List](image)
rings and heteroatom-containing ring structures which were not considered in the first step were added to the basic cores. The addition of four cata-condensed naphthenic rings to the basic cores were allowed at the maximum. Regarding the heteroatom rings, sulfur, nitrogen and oxygen-containing structures were considered, such as thiophene, pyrrole, pyridine, and furan. The maximum number of heteroatom rings contained on a single core was two, and both a combination of different ring structures and a combination of the same ring structure were accepted. As the result of CID FT-ICR MS, it was confirmed that the most of core structures was classified in one-heteroatom classes (N1, O1 and S1 class) or two-heteroatom classes (N2, N1O1, N1S2, O2, O1S1, S2 class). Therefore, the maximum number of heteroatom rings was defined as two in this study.

Finally, core structures were assigned for each mass peak obtained by CID FT-ICR MS by comparing the mass of the observed peaks with the mass of the core structures built in the above two steps. It has reported previously that alkyl side chains added on the core structure could not be dissociated completely in the CID process and the C1 to C4 alkyl-substituted core fragments were detected by CID FT-ICR MS analysis\(^\text{12}\)\(^\text{).}\) This fragmentation behavior was considered in the assignment step. The ratio of assignments for all fractions is shown in Fig. 10. The ratio of assignment was greater than 80\% for all fractions, and the developed method was successful in matching the core structures to the CID peaks. The top ten core structures assigned for the 3A+ and As fractions are shown in Figs. 11 and 12. Naphthalene was the most abundant core structure in the 3A+ fraction, and the two- and three-ring aromatic core structures were major core structures. Sulfur-containing cores were also observed. In contrast, four-ring aromatic core structures were the main type of core in the As fraction, and all of the top ten cores were nitrogen-containing cores consisting of pyrrole and pyridine. Nitrogen-containing compounds were preferentially ionized by LDI, and the parent ions of As fraction contained ions generated from the abundant nitrogen compounds. Therefore, many nitrogen-containing core structures were assigned in this method. The estimated core structures of the
As fraction were compared with typical molecular structures proposed in previous studies\textsuperscript{(20,20,27)}. Two- to four-ring aromatics were major core structures in the archipelago-type As molecules. Four-ring aromatic cores were also assigned at a higher abundance in this study. This comparison shows that the proposed method could provide reasonable core structures for heavy petroleum fractions. The core structure information provided by proposed method would contribute to the accurate characterization of heavy petroleum fractions and the in-depth analysis of the reaction behavior in heavy oil upgrading processes.

4. Conclusion

Detailed analysis of VR samples was performed by a combination of FT-ICR MS analysis and a separation technique. The hetero class distribution and DBE and C# distributions were compared for each fraction, and these distributions indicate the characteristics of each fraction differentiated by aromatic ring number and polarity. To obtain the masses of the core structures, CID FT-ICR MS analysis was performed for each sample. The change in the C# distribution indicates that the dealkylation of the parent ions was induced by CID. In addition, a change in the DBE distribution indicates that the dissociation of the internal linkage of the parent ions had occurred, suggesting that archipelago-type molecules were contained in 3A+ and As fraction. Based on these results, the core structure estimation method was proposed. This proposed method enabled us to assign a core structure to each detected fragment ion successfully. Thus, information about the core structures in heavy petroleum feedstocks can be obtained by a combination of separation techniques: CID FT-ICR MS analysis and the proposed method. In summary, there are two types of molecules, island and archipelago, in heavy petroleum feedstocks, and their reactivity and physical properties are different. The estimation of their compositions and the construction of molecular structures of both molecules will be the subject of future work.

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要  旨

フーリエ変換イオンサイクロトロン共鳴質量分析による重質油成分のコア構造解析

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重質留分中に含まれる分子のコア構造をフーリエ変換イオンサイクロトロン共鳴質量分析（FT-ICR MS）により推定する方法を開発した。スペクトラムとFT-ICR MSを組み合わせ、中東系涯

圧残油中に含まれる分子構造を解析した。さらに、3環以上芳

香族分（3A＋）とアスファルテン分（As）について、衝突誘

起解離（CID）法によるフラグメントーションをFT-ICR MSと組み合わせた解析（CID FT-ICR MS）を実施し、各サプル中

に含まれる分子のコア構造に関する解析を実施した。CID前後の

二重結合等量値（DBE）分布の変化からコア構造間の結合が

解離していることが確認され、3A＋フラクション、Asフラク

ションともに分子内に複数のコア構造が存在する群島型分子が

存在していることが示唆された。最後に、本研究にて提案した

方法を用いてコア構造の推定を行ったところ、CID FT-ICR MS

で得られた各フラグメントイオンに対してコア構造を帰属する

ことができた。Asフラクションで推定されたコア構造は既往の

研究において提案されたアスファルテン分子中に含まれるコ

ア構造と類似のコア構造を示していた。この結果は、本法の妥

当性を示唆しているものと考える。

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