Quantitative Measurement of Retained Oil in Organic-Rich Shale—A Case Study on the Chang 7 Member in the Ordos Basin, China

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This study proposes a method to calculate the retained oil content \( W_O \) in cores collected by a sealed tool from organic-rich shale with thermal maturity around \( \% \text{Ro} = 0.8 \) in the Ordos Basin, China. Approaches such as soaking cores at low temperature, multiple extractions, multiple pyrolysis, and multiple chromatographic analyses were conducted and then the relationships between total retained oil content and mineral compositions were analyzed. The total retained oil content measured by the method proposed in this paper is 60–260% higher than that measured by a conventional pyrolysis method and 34–69% higher than the sum \( W_{O3} + W_{O4} \) of two extractions with dichloromethane \( W_{O3} \) and chloroform \( W_{O4} \). After extractions with dichloromethane and chloroform \( W_{O5} \), the oil retained in the organic-rich shale was 4.7–11.6%, which has not been extracted. Positive correlations exist between \( W_O \) (i.e., \( W_{O3} + W_{O4} \)) and total organic carbon (TOC) and \( S_1 \) (absorbed hydrocarbon by rock pyrolysis), and \( W_O \) has the highest correlation coefficient with the former. The method can provide important guidance for the objective analysis of retained oil in organic-rich shale, and it is reliable for the evaluation of shale oil reserves.

Keywords: organic-rich shale, retained oil, oil content calculation, pyrolysis, sealed coring

INTRODUCTION

Since the groundbreaking progress made by the United States on shale oil in Bakken reserves in the 1950s, technology related to shale oil in the US has been developing rapidly and achieved its profitability in 2018 (Soeder, 2018; Hackley et al., 2020; Solarin et al., 2020; Ulrich-Schad et al., 2020). Drawing lessons from the experience of the USA's shale oil development, China began to explore the technology and practice on shale oil exploration and development and made a step forward on fields including geological theory, exploration and development technology, and experimental techniques (Hou et al., 2020; Hou et al., 2021a; Kang et al., 2020; Ma et al., 2020a; Ma et al., 2020b; Zhao et al., 2020a; Zhu et al., 2021). However, more researches are needed to tackle problems related to the quantitative evaluation of the total retained oil content, the occurrence mechanism of shale oil, and pores and fluid flowing mechanism in shale formation. Among these topics, objective quantitative evaluation on the retained oil content of organic-rich shale has always been the focus of ongoing researches (Jarvie, 2012; Chen and Jiang, 2016; Abrams et al., 2017; Jiang et al., 2017; Li M. W. et al., 2019).
There are two methods commonly used to measure the total retained oil in organic-rich shale: one is conventional chloroform bitumen “A” and the other is rock pyrolysis (Stroup, 1987; Johannes et al., 2007; Han et al., 2015; Nady and Hammad, 2015; Li J. B. et al., 2019). Because light hydrocarbon is easily lost, part of the hydrocarbons in $S_1$ is regarded as residual hydrocarbon. Besides, conventional chloroform bitumen “A” can hardly reveal whether the shale oil is free or absorbed. The other method is modified pyrolysis (Zink et al., 2016; Chen et al., 2017; Li et al., 2018; Li M. W. et al., 2019; Ma et al., 2019; Hou et al., 2021b). In conventional source rock pyrolysis, $S_1$ represents the residual hydrocarbon in rock, which is the oil that has already existed, and $S_2$ represents the hydrocarbon potential in kerogen. In shale oil evaluation, since $S_1$ has compositions similar to shale oil, they can be easily extracted by dichloromethane with weak polarity. Therefore, they are treated as free shale oil. However, $S_1$ does not represent all free shale oil and $S_2$ does not completely show the hydrocarbon potential in kerogen (Chen et al., 2018; Li et al., 2018; Li M. W. et al., 2019; Ma et al., 2019; Hou et al., 2020). $S_2$ contains small amounts of free oil and absorbed oil, so the pyrolysis method cannot estimate the content of absorbed shale oil.

The modified method requires instantly freezing cores by liquid nitrogen in the field (at $-50^\circ$C) and then crushing them in a closed system ($190^\circ$C). Pyrolysis analysis immediately follows. A light hydrocarbon restoring coefficient is estimated by forward modeling, and correction to the historical data of the shale with medium–high maturity is conducted. Absorbed oil can be separated from the already generated hydrocarbon oil by changing the heating rate. But this method still shows limitations in the following aspects: firstly, online analysis cannot be achieved as crushed samples enter the pyrolysis apparatus, resulting in a partial loss of light hydrocarbon. Secondly, the assumption that kerogen generates hydrocarbon at above $300^\circ$C lacks a reliable scientific proof. Besides, since there are only a few samples (in total 100 mg), a big error may exist. For shale with abundant organic matter [total organic carbon (TOC) as high as 20–30% and hydrocarbon potential up to 100 mg/g rock], the error is noticeably high (the maximum $S_2$ of a standard sample in China is 16.98 mg/g rock).

**SAMPLES AND METHODS**

Eleven samples from Well L85 drilled in the Chang 7 member in the Ordos Basin were collected (see basic geochemical information listed in Table 1). After taken into a sealed tool, the cores were wiped with cotton to remove the sealing fluid on their surface within 1.5 h so that they will not be eroded by the sealing fluid. Then, the cores are weighed and put into containers filled with dichloromethane solution. The cores should be completely submerged into the solution by at least 2 cm below. Finally, the containers (i.e., sealed bottles) containing the dichloromethane solution and cores were put into a freezer where the temperature remained below $20^\circ$C to prevent the dichloromethane solution from evaporating (the boiling point of dichloromethane is $39.5^\circ$C). After all these were done, the samples were moved from the field to the laboratory.

After immersing the cores for 10–30 days, 5 ml of methylbenzene was added to the bottle as the standard sample. The solution was placed into a crusher and then the crusher put into liquid nitrogen. The core sample was crushed into particles of 0.18 mm. The crushed sample and the dichloromethane were moved into a bottle and sealed with a cap, and then chromatographic analysis was immediately started (the above procedure is denoted as step 1). After being immersed for 10–30 days, the core sample was separated from the solution. The solution was measured and then 1 ml solution was taken and put into two flasks (labeled A and B) marked with internal rulers. Quantitative analysis of total hydrocarbon gas chromatography in a flask (A#) was conducted (the above procedure is denoted as step 2). Into another flask (B#), after full evaporation, solvent was add to 1 ml and then chromatographic analysis was conducted (the above procedure is denoted as step 3). The rest of solution was weighed after full evaporation. The rest of the crushed sample was placed into the dichloromethane solution after weighing and extraction. Of the solution, 1 ml was taken after the isochoric process and put into two flasks (labeled C and D) with internal rulers. Quantitative analysis of total hydrocarbon gas chromatography in a flask (C#) was conducted (the above procedure is denoted as step 4). Another flask (D#), after full evaporation, is added with solvent to 1 ml and then chromatographic analysis was started (the above procedure is denoted as step 5). The remaining solution was weighed after full evaporation. A certain amount of the sample powder was take after drying, weighed, and the pyrolysis analysis conducted (the above procedure is denoted as REP 1; the results are listed in Table 2). The remaining sample powder was placed into a chloroform solution after weighing and extraction. The solution was completely evaporated and weighed. Again, a certain amount of dried sample was weighed and rock pyrolysis was conducted (the above procedure is denoted as REP 2). The experiments above were conducted at the National Key Laboratory of Enhanced Oil Recovery, Research Institute of Petroleum Exploration & Development, PetroChina.

**RESULTS AND DISCUSSION**

**Chromatographic Analysis**

Figures 1–5 show the chromatographic analysis of the core samples that went through the above steps 1–5. Taking sample 6 as an example, the calculation process is given in Appendix Table A1. The samples have been completely immersed in dichloromethane solution for 10–30 days before being crushed in liquid nitrogen, and then followed by immediate gas chromatography analysis (Figure 1). The light components remain intact, and a complete series of light hydrocarbons, namely, $nC_5$, $nC_6$, $nC_7$, $nC_8$, and $nC_9$, can be detected. The peak area of $nC_7$ is the largest, and $nC_9$ is the main peak. The powder was separated from the solution after the sample was crushed and immersed for 10–30 days. After the isochoric process, 1 ml of the solution was added into flasks A and B with internal rulers.
TABLE 1 | Basic geochemical data of the experiment samples.

| Sample no. | Depth (m) | TOC (%) | Quartz (%) | Potash feldspar (%) | Plagioclase (%) | Calcite (%) | Dolomite (%) | Siderite (%) | Pyrite (%) | Clay (%) |
|------------|-----------|---------|------------|---------------------|----------------|-------------|-------------|-------------|-----------|---------|
| 1          | 1,576.86  | 6.34    | 23.4       | 1.0                 | 7.9            | 0.0         | 12.1        | 0.0         | 12.4      | 43.2    |
| 2          | 1,579.86  | 32.842  | 21.6       | 5.7                 | 4.6            | 0.0         | 2.4         | 0.0         | 35.9      | 29.8    |
| 3          | 1,580.34  | 6.63    | 20.0       | 3.4                 | 5.1            | 3.3         | 7.5         | 12.1        | 9.7       | 38.9    |
| 4          | 1,581.07  | 20.87   | 16.7       | 4.3                 | 7.1            | 0.0         | 7.1         | 0.0         | 36.3      | 28.5    |
| 5          | 1,581.91  | 25.77   | 29.9       | 1.8                 | 1.8            | 0.0         | 1.6         | 0.0         | 31.3      | 33.6    |
| 6          | 1,583.47  | 37.86   | 23.6       | 2.5                 | 1.0            | 0.0         | 5.7         | 0.0         | 32.8      | 34.4    |
| 7          | 1,584.91  | 18.6    | 30.9       | 6.0                 | 3.3            | 4.2         | 3.6         | 0.0         | 42.0      | 10.0    |
| 8          | 1,586.23  | 18.83   | 37.8       | 1.5                 | 6.2            | 0.8         | 1.9         | 0.0         | 15.5      | 44.4    |
| 9          | 1,587.85  | 13.09   | 29.9       | 1.5                 | 5.8            | 0.4         | 1.0         | 0.0         | 10.1      | 22.0    |
| 10         | 1,589.25  | 18.67   | 26.1       | 3.1                 | 4.0            | 4.9         | 6.4         | 0.0         | 35.7      | 19.8    |

TOC, total organic carbon.

TABLE 2 | Pyrolysis results of samples after various treatments.

| Sample no. | Depth (m) | s01 (mg/g) | s02 (mg/g) | tmax0 (°C) | s11 (mg/g) | s12 (mg/g) | tmax1 (°C) | s21 (mg/g) | s22 (mg/g) | tmax2(°C) |
|------------|-----------|------------|------------|-------------|------------|------------|-------------|------------|------------|-------------|
| 1          | 1,576.86  | 3.75       | 15.66      | 440         | 0.24       | 12.80      | 439         | 0.17       | 10.23      | 441         |
| 2          | 1,579.86  | 7.39       | 149.38     | 439         | 0.74       | 137.96     | 437         | 0.60       | 129.70     | 436         |
| 3          | 1,580.34  | 5.39       | 30.77      | 443         | 0.19       | 13.83      | 441         | 0.15       | 13.47      | 444         |
| 4          | 1,581.07  | 10.05      | 87.20      | 442         | 0.86       | 82.84      | 442         | 0.55       | 79.71      | 441         |
| 5          | 1,581.91  | 8.19       | 105.41     | 438         | 1.06       | 95.40      | 436         | 0.67       | 91.93      | 439         |
| 6          | 1,583.47  | 13.33      | 150.92     | 440         | 0.77       | 137.57     | 440         | 0.66       | 132.20     | 442         |
| 7          | 1,584.91  | 9.89       | 70.54      | 441         | 1.50       | 57.73      | 439         | 0.61       | 51.34      | 442         |
| 8          | 1,586.23  | 5.25       | 79.98      | 441         | 0.89       | 61.14      | 442         | 0.57       | 57.64      | 442         |
| 9          | 1,589.85  | 4.07       | 95.89      | 440         | 0.93       | 87.99      | 439         | 0.68       | 82.75      | 440         |
| 10         | 1,591.89  | 4.21       | 70.88      | 441         | 0.69       | 64.29      | 437         | 0.61       | 60.06      | 436         |
| 11         | 1,592.25  | 5.51       | 64.86      | 439         | 0.49       | 55.81      | 439         | 0.38       | 46.47      | 436         |

Quantitative analysis of total hydrocarbon gas chromatography was directly conducted for flask A (see the result in Figure 2). Light hydrocarbons are lost as the immersion time increases (Figure 2). Among them, all of C5 is lost, and the losses of nC6 and nC7 are 52.58 and 26.64%, respectively. C8 and later hydrocarbons gradually increase, and WO1 is calculated to be 0.032 kg/t rock. In Figure 2, toluene and D-C24 standard samples are used for compound calibration. The results show that the error of the two types of standard samples for normal alkanes is 13.55%, and the calibration value of D-C24 is slightly higher, indicating that these two standard samples can be used. Solvent was added into flask B to 1 ml after fully evaporating and then chromatographic analysis proceeded (see the result in Figure 3). After the rock soaking solution volatilized completely at room
FIGURE 2 | Chromatogram of samples that were crushed first and then soaked (chromatogram after step 2).

FIGURE 3 | Chromatogram of samples that were soaked first and then evaporated (chromatogram after step 3).

FIGURE 4 | Chromatogram of samples after dichloromethane extractions (chromatogram after step 4).
temperature, the hydrocarbons before \( nC_{13} \) are almost lost. The results show that the losses of \( nC_{13} \), \( nC_{14} \), and \( nC_{15} \) are 46.76, 14.57, and 0.43%, respectively. The two calculation results of \( nC_{16} \)–\( nC_{25} \) are within +10%. Light hydrocarbons before \( C_{14} \) were quantitatively analyzed by chromatography. The pre-\( C_{14} \) hydrocarbons precipitated by sample soaking are 1.91 kg/t rock, accounting for 32.51% of the total hydrocarbons.

The samples were placed into the dichloromethane solution for extraction after separating the solution from the crushed sample. One milliliter of the extracted solution was collected and placed into flasks C and D with internal rulers after the isochoric process. Quantitative analysis of total hydrocarbon gas chromatography was directly conducted in flask C (similar to flask A) (see the result in Figure 4). The shales were soaked in dichloromethane and then extracted. The extraction product is divided into two parts: one part is that of hydrocarbons after \( C_{10} \) and the other part is of the isomeric hydrocarbons of \( C_6 \)–\( C_7 \) (Figure 4). The molecular radius of this part of the hydrocarbons is small. The hydrocarbons in this part are stored in the shale nanopores and cannot be completely precipitated.
by the dichloromethane. One milliliter solvent was added into flask D after fully evaporating and chromatographic analysis was conducted (similar to flask B) (Figure 5). The D volumetric flask is not easy to volatilize completely during the experiment, so the storage time is very long. Due to the long storage time, the normal alkanes before \( nC_{17} \) have all been lost. However, the \( C_6-C_7 \) isomeric alkanes in Figure 4 are not significantly reduced in Figure 5. It is speculated that these \( C_6-C_7 \) isomeric alkanes may coexist with resins and asphaltenes and are extremely difficult to volatilize.

### Pyrolysis Analysis

After drying the rock samples, pyrolysis analysis was immediately conducted. The results are denoted as \( S_{01}, S_{02}, \) and \( T_{max0} \) (Table 2). Pyrolysis analysis was conducted for the second time after the samples were extracted by dichloromethane and dried by fully evaporating (after REP 1) (Jiang et al., 2017; Li et al., 2018; Li M. W. et al., 2019; Li J. B. et al., 2019). The results are denoted as \( S_{11}, S_{12}, \) and \( T_{max1} \) (Table 2). After weighing, the remaining sample powder was placed in chloroform solution for extraction. Then, after chloroform evaporated, the samples were weighed and dried (after REP 2). Finally, pyrolysis experiment was done for the third time (Sun et al., 2019; Hou et al., 2020). The results are denoted as \( S_{21}, S_{22}, \) and \( T_{max2} \) (Table 2).

### Calculations of Retained Oil Content in Organic-Rich Shale

We conducted sealed coring to organic shale that has a maturity level of \( \%Ro = 0.8 \) in the Ordos Basin to calculate the total retained oil content. The core sample went through procedures including low-temperature soaking, multiple extractions, multiple pyrolysis, and multiple chromatographic analyses (refer to Section “Samples and Methods” for detailed experiment procedures). This study developed an integrated approach to measuring the total retained oil content in organic-rich shale (Chen and Jiang, 2016; Chen et al., 2018; Li et al., 2018; Li M. W. et al., 2019; Ma et al., 2019; Hou et al., 2020). The workflow is shown as follows (Figure 6).

The detailed calculation process is as follows:

\[
W_{O1} = S_{T1} - S_{T2}
\]

### Table 3 | Calculation of oil content in organic-rich shale.

| Sample no. | Depth (m) | \( W_{O1} \) (kg/t rock) | \( W_{O2} \) (kg/t rock) | \( W_{O3} \) (kg/t rock) | \( W_{O4} \) (kg/t rock) | \( W_{O5} \) (kg/t rock) | \( W_{O} \) (kg/t rock) |
|------------|-----------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| 1          | 1576.86   | 0.015                    | 1.587                    | 3.530                    | 0.372                    | 0.607                    | 6.111                    |
| 2          | 1579.86   | 0.005                    | 6.369                    | 11.984                   | 0.625                    | 1.997                    | 20.980                   |
| 3          | 1580.34   | 0.089                    | 3.557                    | 8.861                    | 0.438                    | 0.632                    | 13.577                   |
| 4          | 1581.07   | 0.059                    | 5.390                    | 9.979                    | 0.620                    | 1.666                    | 17.714                   |
| 5          | 1581.91   | 0.006                    | 4.361                    | 15.882                   | 1.086                    | 2.059                    | 23.394                   |
| 6          | 1583.47   | 0.003                    | 5.876                    | 19.139                   | 0.719                    | 2.357                    | 28.094                   |
| 7          | 1584.91   | 0.092                    | 3.458                    | 8.631                    | 2.518                    | 1.925                    | 16.624                   |
| 8          | 1586.23   | 0.088                    | 4.183                    | 12.093                   | 0.854                    | 1.704                    | 18.922                   |
| 9          | 1589.85   | 0.015                    | 2.354                    | 7.487                    | 1.126                    | 0.593                    | 11.575                   |
| 10         | 1591.53   | 0.022                    | 2.493                    | 7.058                    | 0.165                    | 0.575                    | 10.313                   |
| 11         | 1592.25   | 0.009                    | 4.502                    | 7.861                    | 0.464                    | 1.236                    | 14.072                   |
FIGURE 8 | Relationship between the total retained oil content and the extracted sum of dichloromethane and chloroform.

\[ y = 1.3712x + 1.344 \]
\[ R^2 = 0.9586 \]

FIGURE 9 | Relationship between the total retained oil content and TOC.

\[ y = 0.5752x + 5.3859 \]
\[ R^2 = 0.8242 \]

FIGURE 10 | Relationship between the total retained oil content and \( S_1 \).

\[ y = 1.6679x + 4.809 \]
\[ R^2 = 0.6639 \]
$W_{O1}$ refers to the difference $(C_5-C_7)$ between the core samples after step 2 and after step 1 (in flask A#).

$$W_{O2} = S_{T3} - S_{T2} + W_{V1}$$

$W_{O2}$ refers to the difference $(C_6-C_{14})$ between the core samples after step 3 (flask B#) and after step 2 (flask A#), plus the weight $W_{V1}$ of the evaporated solution remaining after step 2. $S_{T3} - S_{T2}$ refers to the light hydrocarbon in the sample.

$$W_{O3} = S_{T5} - S_{T4} + W_{V2}$$

$W_{O3}$ represents the difference $(C_6-C_{14})$ between the core samples after step 5 (D#) and after step 4 (C#), plus the weight $W_{V2}$ of the evaporated solution remaining after step 5. $S_{T5} - S_{T4}$ refers to the light hydrocarbon in the sample.

The solution, after extracted by chloroform, filtered, and evaporated completely, is weighed to be $W_{O4}$. The hydrocarbons retained in the shale after chloroform extraction is defined as $W_{O5}$, and this part of hydrocarbons can be calculated from Figure 7. After the shale is extracted by dichloromethane and chloroform, the difference of the two pyrolysis $S_1$ values and the amount of chloroform extraction show a positive relationship. Therefore, pyrolysis analysis of the rock after chloroform extraction can infer the retained hydrocarbon content in the rock according to the $S_1$ content.

Therefore, the calculated oil content in shale should include five parts (Table 3), namely:

$$W_O = W_{O1} + W_{O2} + W_{O3} + W_{O4} + W_{O5}$$

The retained oil $W_{O4}$ in organic-rich shale after extracted by dichloromethane and chloroform accounts for 4.65–11.58%. In other words, there is 4.65–11.58% of retained oil that can hardly be soluble in organic solvent in organic-rich shale, and this part of retained oil can hardly be extracted.

**Correlation Analysis of Geochemical Parameters**

The total retained oil content shows good correlations with the extracted sum of dichloromethane and chloroform, whose correlation coefficient is $R^2 = 0.96$ (Figure 8). This phenomenon illustrates that the primary components in the total retained oil are mainly soluble organic matter that can be extracted by dichloromethane and chloroform. In other words, the retained oil in organic-rich shale can be extracted using some techniques.

A positive correlation between the total retained oil content and TOC exists, with $R^2 = 0.82$ (Figure 9). This phenomenon demonstrates that the increase in TOC may cause more shale oil remaining in rock, namely, retained oil (Hou et al., 2020; Shao et al., 2020; Zhao et al., 2020b). To explore shale oil, shale with a higher TOC is the target.

A positive correlation exists between the total retained oil content and $S_1$ (Chen et al., 2017; Chen et al., 2018; Li et al., 2018; Li M. W. et al., 2019; Ma et al., 2019). The correlation coefficient is $R^2 = 0.66$ (Figure 10). The relatively weak correlation also shows that the retained oil in shale cannot be calculated objectively only by the method of conventional rock pyrolysis.

**CONCLUSION**

This study took sealed cores of organic-rich shale in the Ordos Basin and measured the total retained oil ($W_O$) via approaches including low-temperature soaking, multiple extractions, multiple pyrolysis, and multiple chromatographic analyses. The $W_O$ value obtained from the new method is 60–260% higher than that obtained from conventional pyrolysis and 34–69% higher than the sum of the extractions by dichloromethane ($W_{O3}$) and chloroform ($W_{O4}$). Even after extraction by dichloromethane and chloroform, there remains 4.7–11.6% hydrocarbon retained in the organic-rich shale ($W_{O5}$). The total retained oil content ($W_O$) in the organic-rich shale exhibits a positive relationship with the sum of the extractions using dichloromethane and chloroform ($W_{O3} + W_{O4}$), with $R^2$ reaching 0.96. This indicates that the primary composition in the total retained oil is soluble organic matter and is extractable via dichloromethane and chloroform. Positive correlations can also be observed between $W_O$ and TOC, and $S_1$ through coefficients of 0.82 and 0.66, respectively.

**DATA AVAILABILITY STATEMENT**

The original contributions presented in the study are included in the article SUPPLEMENTARY MATERIAL, further inquiries can be directed to the corresponding author/s.

**AUTHOR CONTRIBUTIONS**

LH: conceptualization, methodology, investigation, and writing — original draft. XL: data curation, writing — review and editing. SL: formal analysis, resources. ZZ: software, validation, and project administration. YL: funding acquisition. All authors contributed to the article and approved the submitted version.

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### APPENDIX

#### TABLE A1 | Typical chromatogram table of sample 6 and the calculation process.

| Hydrocarbons | Peak area | Calculation process |
|--------------|-----------|---------------------|
|              | Step 1    | Step 2: toluene SS (mg) | Step 2: (D-C24 SS (mg)) | Step 3 | Step 4 | Step 5 | Step 2 - Step 1 | Step 3 - Step 2 |
|              | Step 2: (D-C24 SS (mg)) | Step 3 | Step 4 | Step 5 | Step 2 - Step 1 | Step 3 - Step 2 |
| nC5          | 129.234   | 6.851              |                  |          |          |          |                 |                 |
| nC6          | 104.583   | 7.323              | 1.636            |          |          |          |                 |                 |
| nC7          | 142.175   | 15.388             | 1.844            |          |          |          |                 |                 |
| Toluene      | 245.039   | 36.152             | 19.204           | 12.990   | 12.990  | 15.027  | 8.704            | 0.000            |
| nC8          | 81.334    | 23.456             | 1.656            | 4.312    | 8.428   | 9.750   | 0.750            | 95.472           |
| nC9          | 80.899    | 33.309             | 4.488            | 4.289    | 11.968  | 13.845  | 2.034            | 179.075          |
| nC10         | 60.581    | 40.674             | 8.974            | 3.212    | 14.615  | 16.907  | 4.068            | 355.075          |
| nC11         | 52.359    | 36.367             | 11.264           | 2.776    | 13.067  | 15.116  | 5.105            | 370.781          |
| nC12         | 36.814    | 26.661             | 10.615           | 1.952    | 9.580   | 11.082  | 4.811            | 390.870          |
| nC13         | 25.254    | 24.416             | 11.724           | 1.399    | 8.773   | 10.149  | 5.014            | 555.311          |
| nC14         | 22.129    | 24.507             | 18.885           | 1.173    | 8.806   | 10.187  | 8.70             | 550.639          |
| nC15         | 20.682    | 29.183             | 26.211           | 14.538   | 1.096   | 10.486  | 12.130           | 6.589            | 856.402          |
| nC16         | 18.202    | 22.812             | 21.728           | 13.022   | 0.015   | 9.665   | 8.197            | 9.482            | 10.01            | 5.902            | 0.018            | 749.468          | 5.594           |
| nC17         | 13.572    | 22.674             | 21.333           | 13.304   | 2.304   | 0.719   | 8.147            | 9.425            | 9.83             | 6.030            | 2.767            | 1,022.367        | 4.305           |
| nC18         | 12.974    | 21.677             | 20.607           | 12.443   | 3.802   | 0.682   | 7.789            | 9.010            | 9.50             | 5.640            | 4.566            | 1,041.270        | 5.390           |
| nC19         | 10.535    | 21.434             | 20.233           | 15.074   | 3.634   | 0.558   | 7.702            | 8.909            | 9.32             | 6.832            | 4.36             | 1,279.023        | 4.650           |
| nC20         | 9.359     | 16.853             | 16.331           | 9.943    | 3.737   | 0.496   | 6.056            | 7.005            | 7.53             | 4.507            | 4.488            | 1,120.536        | 7.428           |
| nC21         | 6.793     | 16.126             | 15.045           | 9.457    | 3.229   | 0.380   | 5.794            | 6.703            | 6.93             | 4.286            | 3.878            | 1,509.044        | 3.430           |
| nC22         | 5.757     | 13.167             | 12.343           | 8.366    | 3.258   | 0.305   | 4.731            | 5.473            | 5.69             | 3.792            | 3.913            | 1,450.221        | 3.924           |
| nC23         | 4.752     | 10.261             | 9.259            | 6.302    | 2.372   | 0.252   | 3.887            | 4.265            | 4.27             | 2.856            | 2.849            | 1,363.579        | 0.036           |
| D-C24        | 5.389     | 4.861              | 4.942            | 6.528    | 1.936   | 2.240   | 1.936            | 2.240            | 2.24             | 7.84             | 0.000            |                  |                 |
| nC24         | 3.969     | 7.392              | 6.956            | 4.545    | 1.334   | 0.210   | 2.666            | 3.073            | 3.21             | 2.060            | 1.602            | 1,162.362        | 4.323           |
| nC25         | 3.124     | 6.122              | 5.529            | 3.729    | 1.102   | 0.166   | 2.200            | 2.545            | 2.55             | 1.690            | 1.323            | 1,228.266        | 0.305           |
| nC26         | 2.623     | 5.933              | 3.321            | 3.298    | 0.139   | 2.132   | 2.466            | 1.53              | 1.495            | 0               | 1,433.130        |                  |                 |
| nC27         | 3.72      | 1.888              |                  | 1.337    | 1.546   | 0.854   | 0               | 0               | 0               | 0               | 0               | 0               | 0               |
| nC28         | 1.826     | 0.701              |                  | 0.666    | 0.759   | 0.318   | 0               | 0               | 0               | 0               | 0               | 0               | 0               |
| Before nC8   | 1,334.078 | 185.257            |                  | 70.722   | 66.566  | 77.004  | 0               | 0               | 0               | 0               | 0               | 0               | 0               |
| Before toluene | 2,376.689 | 696.425            | 86.998           | 186.434  | 125.993 | 250.237 | 289.477         | 40.09            | 84.503           | 0               | 0               | 0               | 0               |
| Before       | 52.553    | 43.952             |                  | 23.820   | 24.696  | 0               | 0               | 0               | 0               | 0               | 0               | 0               | 0               |