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Research Article

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The application of GC in the study of the effect of oil spill dispersant

Wang Qiaomin, Yan Zhiyu*, Sun Bing, Zhu Xiaomei and Liu hui

Environmental Science and Engineering College, Dalian Maritime University, No.1 Linghai Road, Dalian, China

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ABSTRACT

The effect of the oil spill dispersant (OSD) in the laboratory is mostly evaluated by testing the emulsification of the OSD at present. Test value of dispersing effect in the laboratory is generally higher than the value in the actual field. Mainly because a part of the spraying oil spill dispersants (OSDs) directly get into the water without a full role with the spilled oils, which not only reduces the overall dispersion effect, but also increases the cost of handling the oil spill and the secondary contamination to marine environment. Therefore, the total number of the OSDs that actually exists in the oil should be considered to evaluate the effect of a certain OSD, and the miscibility of the oil with the OSD should also be considered. Aim at the demand for testing the total number of the OSDs in the oil, this study has explored the feasibility of an analytical method of the total number of the OSDs in the oil using the gas chromatography (GC). First, the characteristic peaks representing these two substances in the GC had been found. Secondly, standard curves were made with the relationship between the two characteristic peak ratios and the mass ratios. Finally, the most appropriate characteristic peaks of the OSD and the oil were selected, with which a better standard curve was also selected, considering the role of weathering at the same time, which are used to test the relative total number of the OSDs in the oil spill.

Key words: Oil spill dispersant; Gas chromatography; Analysis

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INTRODUCTION

Oil spills happening frequently in the marine environment are directly related to the increasing of the usage number of the oils in the energy field. Despite the international agreements on oil pollution have many strict prevention strategies, but the large-scale oil spills still occurred frequently [1]. The surfactant in the OSDs can effectively lower the interfacial tension between the oil and the water, thus greatly speeding up the oil spill dispersing into the water [2], due to which the OSDs frequently are used to handle the oil spills. In order to better select the more appropriate OSD, a number of standardized laboratory tests are often used to evaluate the effect of different kinds of the OSDs [3]. Fingas [4] reported that there are about 50 different laboratory test methods can be used to test the dispersing ability of the OSDs. These tests in laboratory scale are in a controlled environment. The results show that all the OSD effect values in the laboratory were higher than in the actual field, which is mainly because the surfactant is separated from the spilled oils during the initial usage period or the mixing period after the spraying, that is straightforward physical loss, the hydrophilic part of the surfactant directly losses into the water, and the removal of surfactants was equivalent to a proportional loss of the entire dispersant [5]. For that reason, the accurate effect of the OSD is depended on the actual number of the OSDs in the oils instead of the total number of the OSDs that have been used. Therefore, determining the actual number of the OSDs in the oil spills under different conditions is a new focus of the OSD's effect, which overcomes the former shortcomings that only considering emulsifying efficiency of the OSD, is a kind of supplement and improvement to the evaluation of the OSD, and is also an important means to determine whether the OSD is physical loss directly. Based on such demand, this study has explored the feasibility of GC to analyze the actual relative number of the OSDs in the oil spill, which can be provided to evaluate the effect of the OSD more accurately and objectively. The reproducibility of the data had been ensured by several parallel measurements, and the oil's and the OSD's most appropriate characteristic peaks were determined by considering the effects of weathering , reliable and stable standard curve obtained at the same time providing the experimental data and means for determining the actual relative number of the OSDs in the oil spill.

EXPERIMENTAL SECTION

The experimental oil is from a platform in Bohai. The OSD is the FuKen-Ⅱ OSD from Qingdao Huahai Environmental Protection Industry Co., Ltd, which is composed mainly of high purity oil-based and non-ionic surface active agents (oxidized lipids), coupler and penetrating agent. The emulsification is that: 30s, > 60%; 10min, > 20% with the using range of 20% -70% in the oils. Experimental sample is a kind of mixture of the OSD and the oil. The quality ratio of the OSD and the oil (expressed by m_D/m_O) is 0, 0.1, 0.2, 0.4 and 0.6. The GC is the Shimadzu Co. 2010 gas chromatography.

2.1 Pretreatment

The chromatography column was successively filled by cotton, 5.5g silica gel with column chromatography reagent grade (100-200 mesh, activation for 5 hours at 120℃), and 1.2g anhydrous sodium sulfate (AR, activation for 12h at 30℃) placed on the top. Each sample accurately weighed was fully dissolved by 15mL configured mixed solution of dichloromethane and n-hexane (volume ratio is 2:1). Rinse the filled column by 10mL hexane, when anhydrous sodium sulfate just exposed, immediately pouring the dissolved oil sample prepared into the column and collecting the chromatography liquid for testing.

2.2 Testing conditions of the GC

The temperature of the inlet and the detector were respectively 280℃ and 300℃, and the carrier gas was high purity N_2. Temperature program was that: the initial temperature was 60℃ at first, then increased to 100℃ by 20℃/min, keeping for 2 min; and then increased to 280℃ by 8℃/min, keeping for 50 min.

To facilitate discussion of the experiment, the peak height values of the OSD and the crude oil were respectively represented by D_i and O_j, where D and O represented the OSD and crude oil, and i and j were the subscripts representing the retention time of the OSD and the oil respectively with the units were min. For example, $D_{8.91}$ refers to the OSD's peak height value at the retention time of 8.91min and $O_{3.2}$ refers to the oil's peak height value at 3.2min.

RESULTS AND DISCUSSION

3.1 The selection of the OSD's and the oil's characteristic peaks

The crude oil is a complex mixture composed of multiple ingredients. When the oil mixes with the OSD, there is a significant problem that whether a single peak of GC can represent the overall and how it to be used in quantitative analysis for the crude oil. In this study how the characteristic peaks are selected is the critical step. The selection principle here is the first consideration problem and a multiple of the OSD's and the oil's characteristic peaks are selected at first to avoid singularity, randomness, inaccuracies and specificity. The appropriate peak selected is shown as follow based on the gas chromatograms of the Bohai crude oil and the OSD shown in Fig.1 and Fig.2 respectively.

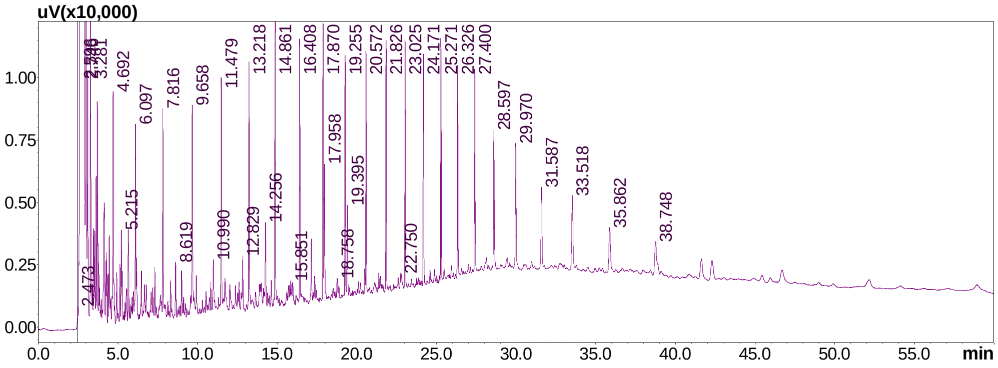

Fig.1 The gas chromatogram of the Bohai oil

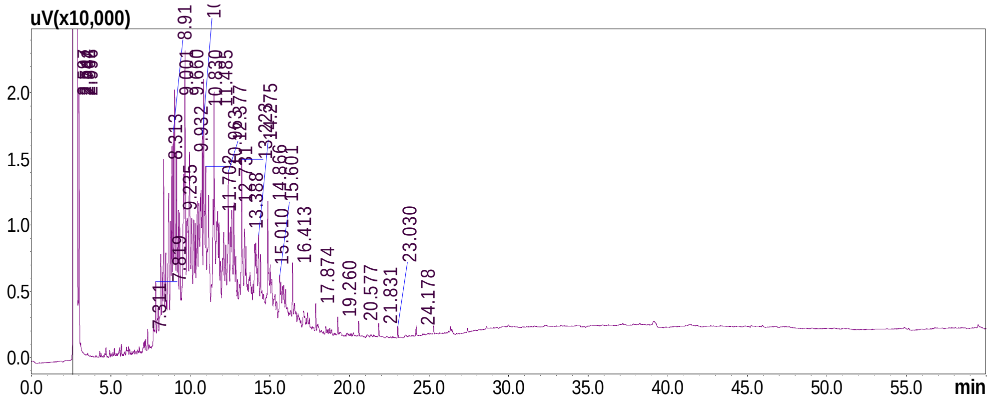

Fig.2 The gas chromatogram of the OSD

Compared the gas chromatogram of the oil with that of the OSD, it can be found that the retention time range of the OSD (mainly 7-24min) is contained in the retention time range of the oil (mainly 3-38min). The adjacent peaks of the oil and OSD are divided into three categories depending on their relative strength: ①the OSD's peaks are strong, while the oil's peaks are weak (the former is 3-5 times than the latter); ② the OSD's peaks are weak, while the oil's peaks are strong (the latter is 3-5 times than the former); ③ the OSD's and oil's peaks are almost the same. The peaks in ① and ② are tentatively defined as OSD's and oil's characteristic peaks respectively in the study.

Namely: when the retention time is 8.91, 8.99, 9.6, 10.8, 11.4, 12.3 or 15.0min, the corresponding maximum peaks are the OSD's characteristic peaks. When the retention time is 3.2, 4.6, 5.6, 6.09, 16.4, 17.8, 19.2, 20.5, 21.8, 23.0, 24.1, 25.2, 26.3, 27.4, 28.5, 29.9, 31.5, 33.5, 35.8 or 38.7 min, the corresponding maximum peaks are the oil's characteristic peaks based on Fig.1 and Fig. 2.

Table 1 The relative standard deviation (RSD) of D_i/O_j in the sample of the OSD and the oil with various ratios

Th D RS O_j	$D_{8.91}$	$D_{8.99}$	$D_{9.6}$	$D_{10.8}$	$D_{11.4}$	$D_{12.3}$	$D_{15.0}$
$O_{3.2}$	5.68%-28.74%	5.68%-28.28%	7.92%-29.51%	8.11%-28.48%	9.14%-30.19%	9.67%-29.23%	11.29%-29.60%
$O_{4.6}$	1.43%-11.79%	1.73%-7.86%	2.14%-12.92%	2.39%-17.10%	3.61%-18.79%	2.57%-19.78%	7.78%-24.06%
$O_{5.6}$	1.24%-11.64%	0.78%-6.76%	1.71%-11.61%	2.31%-15.88%	3.19%-17.36%	2.99%-18.52%	6.48%-23.30%
$O_{6.09}$	1.36%-12.83%	0.60%-5.94%	1.74%-9.79%	2.77%-14.55%	2.91%-15.31%	2.98%-17.07%	6.94%-22.93%
$O_{16.4}$	3.56%-18.50%	2.22%-11.90%	1.86%-8.15%	2.66%-8.07%	1.83%-6.33%	3.28%-7.84%	2.46%-16.19%
$O_{17.8}$	4.30%-17.87%	2.97%-10.82%	2.73%-8.58%	3.67%-8.07%	2.39%-7.26%	3.80%-7.86%	5.78%-17.42%
$O_{19.2}$	6.60%-17.90%	5.66%-11.31%	5.38%-9.01%	5.38%-8.67%	2.95%-7.76%	5.42%-8.91%	6.56%-20.03%
$O_{20.5}$	7.25%-16.58%	6.90%-10.87%	5.91%-9.75%	5.67%-8.80%	4.28%-8.71%	7.39%-9.05%	7.79%-21.05%
$O_{21.8}$	5.34%-17.31%	5.15%-11.31%	4.37%-9.94%	6.24%-9.80%	4.46%-8.91%	7.43%-10.64%	7.28%-23.15%
$O_{23.0}$	5.84%-17.27%	5.71%-12.92%	5.09%-12.83%	6.05%-12.46%	5.15%-11.75%	7.59%-12.74%	8.53%-23.63%
$O_{24.1}$	7.33%-16.42%	7.13%-15.08%	6.89%-14.81%	5.22%-14.55%	5.03%-13.50%	6.51%-14.74%	10.51%-21.47%
$O_{25.2}$	6.80%-16.81%	5.52%-16.10%	4.91%-15.77%	5.43%-15.59%	4.69%-14.45%	6.28%-15.75%	11.00%-20.75%
$O_{26.3}$	4.54%-17.86%	2.95%-17.92%	2.37%-17.46%	3.84%-17.32%	5.96%-24.53%	5.33%-17.42%	10.73%-22.46%
$O_{27.4}$	5.45%-16.86%	4.06%-16.77%	3.57%-16.02%	4.79%-15.79%	3.27%-14.37%	6.02%-15.90%	11.17%-20.45%
$O_{28.5}$	5.37%-18.26%	3.94%-18.04%	3.48%-17.19%	4.44%-16.90%	3.49%-15.51%	5.67%-17.03%	11.93%-21.21%
$O_{29.9}$	7.13%-20.19%	6.34%-20.15%	6.33%-19.37%	7.12%-19.14%	6.30%-17.73%	8.49%-19.16%	10.85%-23.48%
$O_{31.5}$	7.44%-23.56%	7.09%-23.57%	6.90%-22.62%	7.67%-22.24%	6.85%-20.81%	8.69%-22.21%	11.16%-25.49%
$O_{33.5}$	7.16%-19.94%	7.15%-19.71%	7.75%-18.63%	7.60%-18.32%	7.88%-16.85%	8.78%-18.32%	9.54%-24.58%
$O_{35.8}$	7.02%-21.63%	6.46%-21.60%	6.99%-20.63%	6.90%-20.01%	7.12%-18.80%	8.08%-20.02%	11.08%-22.68%
$O_{38.7}$	7.06%-20.66%	7.01%-20.58%	8.86%-19.35%	9.56%-18.73%	10.30%-17.42%	10.63%-18.59%	10.87%-20.51%

3.2 The assurance of experimental data

Before the standard curve is made by using the above characteristic peaks, the characteristic peaks picked above will be selected initially based on parallel sample analysis repeatability to ensure the quality of the data. The variables and the dependent variables of the standard curve are respectively the ratio of quality (m_D/m_O) and the peak height (D_i/O_j). The range of the relative standard deviation is calculated in Table 1.

According to table 1, if the value of the relative standard deviation is greater than 10%, the peaks will be discarded, from which the desirable characteristic peaks are obtained. The OSD's characteristic peaks are the ones whose retention time are 9.6, 10.8 and 12.3min, similarly the oil's characteristic peaks are the ones whose retention time are

16.4, 17.8, 19.2, 20.5 and 21.8min. Most of the ratios above are steady, which can confirm that the single peak can represent the whole amount. Some of ratios are less stable, impacting the accuracy of the data is probably due to the loss of volatile low-carbon substances, or the difficulty of gasification for high carbon material in the gasification chamber of the GC.

3.3 The drawing of the standard curve

The standard curve was made with the ratios of characteristic peak height selected above, whose mutual interference are small and reproducible are good, to further determine whether the single peak ratios can represent the overall quality ratio in the oil-OSD mixture. and the D_i/O_j is calculated of the samples with m_D/m_O = 0,0.1,0.2,0.4,0.6 (where i = 9.6,10.8 and 12.3 min; j = 16 4,17.8,19.2,20.5 and 21.8 min.). Each of the above D_i/O_j corresponding m_D/m_O can make one standard curve, so the total number of the curves is 15, each of which has its R^2 value to judge the accuracy of the standard curve. The results are shown in Table 2.

Table 2 The R^2 value of the standard curve

The R^2 value D_i O_j	$O_{16.4}$	$O_{17.8}$	$O_{19.2}$	$O_{20.5}$	$O_{21.8}$
$D_{9.6}$	0.9642	0.9726	0.9766	0.9854	0.9892
$D_{10.8}$	0.9941	0.9945	0.9955	0.9973	0.9981
$D_{12.3}$	0.996	0.9968	0.9975	0.9988	0.9992

From table 2, it can be seen that most of the R^2 value of the standard curve obtained are greater than 0.97, wherein the R^2 values of $D_{10.8}/O_j$ and $D_{12.3}/O_j$ (j = 16. 4, 17.8, 19.2, 20.5 and 21.8 min) are all greater than that of 0.99 min.

3.4 The effect of the weathering

As used to deal with the oil spill in practice, it is need some time for the OSDs to mix with the oil, during which a small number of the oil and OSD will evaporate. It is obvious that in the research of the combination stability of the oil spill and OSD or the effect continuity of the OSD, the weathering impact (mainly evaporation process) should be considered. In theory, if the characteristic peaks are not affected by the weathering in the short term, namely the value of the peak height is not changed, the ratios of the characteristic peak height will be not affected by weathering and still can reflect the initial mass ratio. That is to say, the weathering has no effect on the standard curve. In this study, the short-term weathering experiment is performed in 72h and sampled at 0, 3, 12, 24, 48 and 72h for sample of m_D/m_O = 0.4 , which aim to judge the impact of the weathering on this method. The relative standard deviation of D_i/O_j and the R^2 values of the standard curve are the specific investigation item, wherein D_i/O_j is the ratio of the characteristic peak in the 3.3, i.e. i = 10.8 and 12.3 min, j = 16. 4, 17.8, 19.2, 20.5 and 21.8 min selected above. The result is shown in the table 3.

Table 3 The relative standard deviation (RSD) of D_i/O_j after weathering

The RSD D_i O_j	$O_{16.4}$	$O_{17.8}$	$O_{19.2}$	$O_{20.5}$	$O_{21.8}$
$D_{9.6}$	11.33%	12.99%	12.99%	14.49%	16.45%
$D_{10.8}$	9.00%	10.97%	10.11%	12.04%	14.09%
$D_{12.3}$	7.22%	9.58%	8.68%	11.48%	14.19%

The more appropriate acceptable peak ratios are $D_{10.8}/O_{16.4}$, $D_{12.3}/O_{16.4}$, $D_{12.3}/O_{17.8}$, $D_{12.3}/O_{19.2}$ found from the Table 2 and Table 3. Because the mixture of the oil and OSD is uneven semi-liquid state due to the insufficient mixing. It may have some error in analysis, Even so, the errors above is acceptable.

The effect of the weathering to the ratio of the peak height has been further investigated through the above standard curve showed in Fig.3 and Table 4. The ratio of the characteristic peak height were calculated when m_D/m_O = 0.4, and compared with the actual average ratio of characteristic peak height during the weathering process, all of which is showed in Table 5.

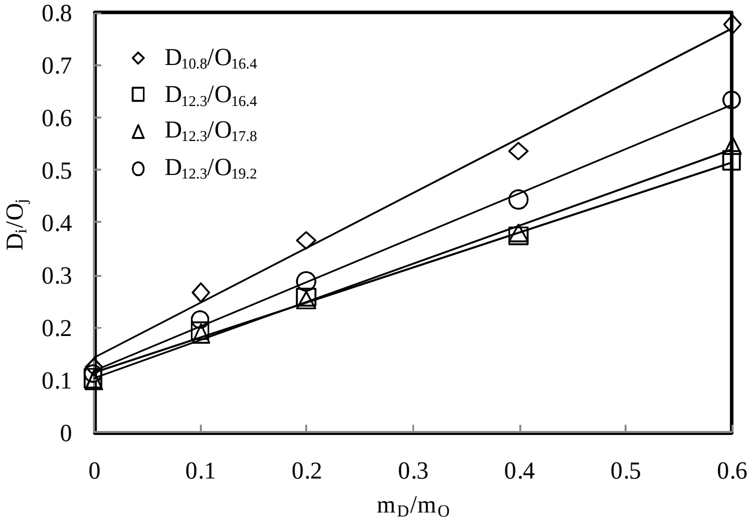

Fig.3 The standard curve of $D_{10.8}/O_{16.4}$, $D_{12.3}/O_{16.4}$, $D_{12.3}/O_{17.8}$ and $D_{12.3}/O_{19.2}$

Table 4 The standard curves in Fig.3 corresponding parameter table

D_i/O_j	$D_{10.8}/O_{16.4}$	$D_{12.3}/O_{16.4}$	$D_{12.3}/O_{17.8}$	$D_{12.3}/O_{19.2}$
The fitting equation	y=1.04x+0.14	y=0.67x+0.12	y=0.73x+0.10	y=0.85x+0.12
The R^2 value	0.9941	0.9960	0.9968	0.9975

Where, y is m_D/m_O, x is D_i/O_j

Table 5 The table of the average of $D_{10.8}/O_{16.4}$, $D_{12.3}/O_{16.4}$, $D_{12.3}/O_{17.8}$ and $D_{12.3}/O_{19.2}$ at six weathering times

D_i/O_j	$D_{10.8}/O_{16.4}$	$D_{12.3}/O_{16.4}$	$D_{12.3}/O_{17.8}$	$D_{12.3}/O_{19.2}$
The average of the weathering	0.5102	0.3759	0.3778	0.4152
The calculated value	0.5606	0.3827	0.3964	0.4569
The relative deviation	9.87%	1.80%	4.94%	10.03%

The relative deviation of the calculated value and the actual value after weathering is almost all less than 10% as showed in table 5. Only the relative deviation of $D_{12.3}/O_{19.2}$ is slightly more than 10%. Therefore, the most appropriate characteristic peak of the OSD is the peak at 12.3min and the most appropriate peak of the oil is the peak at 16.4min according to the above consolidated selecting results. For such most appropriate peaks, the standard deviation of six injections is 3.28% -7.84%, the R^2 value of the standard curve is 0.9960, the value of the relative standard deviation that was affected by weathering is 7.22%, and the relative deviation of $D_{12.3}/O_{16.4}$ between the actual average value and the calculated value is 1.80%. The fitting equation of standard curve is $m_D/m_O = 0.67D_i/O_j +0.12$.

CONCLUSION

Studies on whether the GC is valid to analyze the actual number of the OSDs in the oil are still few in the oil spill field. Under the demand on the new methods and items in the OSD evaluation, this study is pursued here and the feasibility of GC has been explored as follow.

Through chromatographic analysis of the Bohai crude oil and the Fuken -II OSD, the oil's and OSD's characteristic peaks were initially selected depending on the relative strength of adjacent peaks; all the peaks were taken into account to be selected in order to avoid the singularity and specificity of the selected peaks, and then selecting the most appropriate peaks through analysis and test. First, the mixture of the oil and the OSD was configured in different proportions, and the ratio of characteristic peak height of the samples was tested parallel. The more appropriate oil's and OSD's peaks were further selected according to the relative standard deviation of the ratio of the characteristic peaks, which avoided human and testing errors; Secondly, the standard curve was made depending on initial selection of the characteristic peaks, the R^2 value of which can be used for the further selecting. Finally, the mixture of the oil and the OSD weathered for 72h was studied in this study, and the calculated values were also compared with the real measured values. The most appropriate characteristic peaks of the oil and the OSD were obtained, the retention times of which were 16.4 and 12.3 min respectively. Lastly, the standard curve of mass ratio and the most appropriate peak height ratio was made, which was of good repeatability, can represent the total number of the OSD and the oil, and was slight influenced by the weathering. The curve can be used to analyze the actual number of the OSD in the oil spill in this experiment.

This paper provides methods and ideas for the study of the analysis method for OSDs in the spilled oils, and provides a simple and reliable analytical method to enrich and improve the effectiveness evaluation of the OSDs.

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