

Research Progress On Identification Methods And Traceability Experimental Methods Of Oil Spills On The Sea

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Abstract. Oil spill composition is complex and difficult to identify. Traditional oil spill identification techniques include gas chromatography, infrared spectroscopy, liquid chromatography, fluorescence spectrometry, gas chromatography-mass spectrometry and nuclear magnetic resonance spectroscopy. Different methods of oil spill identification have their advantages and disadvantages. Oil spill identification is of guiding significance to the clean-up of oil spill at sea, liability disputes and the subsequent ecological restoration. In order to improve the persuasiveness and reliability of the identification results, it is necessary to combine different identification methods and develop a new oil spill identification technology. Based on the analysis of oil spill types, oil spill identification methods and relevant experimental facilities at home and abroad, it is necessary to carry out research on oil spill identification methods and traceability experiments, so as to provide a reliable basis for legal adjudication of oil spill accidents.

Keywords: Oil spill; oil type identification methods; traceability experiments.

1. Introduction

1.1 The situation of marine environmental pollution is grim

With the development of social economy, human's demand for energy continues to increase, offshore oil exploration and transportation activities are becoming more frequent, the risk of oil spills is increasing.

In recent years, the frequency of oil spill pollution events has been rising rapidly. From 2000 to 2002, about 1~3 oil spill pollution incidents occurred in Bohai Sea every year, with an annual average of 2.3 oil spill incidents. From 2008 to 2010, the annual occurrence of oil spill pollution incidents in Bohai Sea ranged from 4 to 12, with an average annual occurrence of

9.3 oil spill incidents. In 2010, a total of 12 oil pollution incidents were found in the Bohai Sea, all of which were small oil spills, including 10 fuel oil spills related to ship spills. In 2011, a major oil spill occurred in Penglai 19-3 oilfield in the middle of Bohai Sea, which caused serious impact on marine ecological environment and aroused great concern of the state and society. The rapid development of China's marine economy, the construction of coastal oil ship transportation, offshore oil exploration, large oil reserve bases and petrochemical projects,

have intensified the risk of sea oil spill in China, and the disposal of sea oil spill accidents is extremely difficult.

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The 14th Five-Year Plan for Marine Ecological Environment Protection mentioned that China's marine environmental pollution situation is still severe, the improvement of coastal water quality is not stable, some gulf estuaries pollution rebound, offshore oil spills and other sudden environmental incidents are still high; The trend of marine ecological degradation has not been fundamentally curtailed, marine ecological disasters are frequent, and the task of marine ecological protection and restoration remains arduous and complex.

1.2 Relevant national planning puts forward research requirements for oil spill identification

National Plan for the Development of Major Offshore Oil Spill Emergency Response Capability (2021-2035) proposes to "promote research on the identification and traceability technology of unknown source oil spills". The 14th Five-Year Plan for Marine Ecological Environmental Protection proposes to build a national oil fingerprint database for offshore oil spills. It is proposed to establish and improve the identification and assessment technology and standard system of damage to marine ecological environment caused by oil spills, hazardous chemical spills and other emergencies.

1.3 Oil spill identification technology has developed rapidly

At present, the standard used in the identification of offshore oil spills in China is the standard of specifications for identification system of spilled oil on the sea (GB 21247-2007), which has played an important role in the identification of many offshore oil spills in our country, and the identification conclusion is accurate and reliable. With the promotion of these methods and the increase of the frequency of oil spill accidents, GB 21247-2007 also shows some limitations, mainly in that the method is more complex to operate, which is not conducive to large-scale promotion and is not conducive to deal with more frequent oil spill accidents.

2. Analysis And Evaluation Of Research Status At Home And Abroad

2.1 Analysis of the main types of spilled oil on the sea

At present, the main types of spilled oil on the sea in China are crude oil and fuel oil. Crude oil mainly comes from marine oil spill pollution accidents such as blowout of offshore oil platforms, damage of submarine oil pipelines, and leakage of crude oil transport vessels[1]. Fuel oil mainly comes from the leakage caused by ship grounding, collision, rock collision, cabin damage.[2]

According to API gravity, the international oil market usually classifies crude oil into four types: light crude oil, medium crude oil, heavy crude oil and extra heavy crude oil.[3]

Fuel oil is black and viscous, containing more non- hydrocarbon compounds, colloid and asphaltene. Fuel oil consists of heating oil and heavy fuel oil two categories. Heavy fuel oil is the main fuel used in ships at present. The common models are the kinematic viscosity of 120, 180 and 380 mm²/s respectively.

2.2 Research progress of spilled oil identification methods

It is difficult to distinguish crude oil from fuel oil because common fuel oil is similar to heavy crude oil in terms of physical and chemical properties[4]. With the frequent occurrence of offshore oil spill accidents of unknown source, the requirement of identification is more urgent in oil spill accidents.

The existing oil identification methods mainly include physical index identification and chemical fingerprint identification.

2.2.1 physical index identification method

The identification method of physical index mainly includes distillation range method, density/viscosity method and element content identification method.

2.2.1.1 Distillation range method

Crude oil is a mixture of a variety of hydrocarbons, containing heavy hydrocarbons and a certain amount of light hydrocarbons. Fuel oil is a petroleum product made by separating light components from crude oil, or by adding light oil such as diesel to heavy fuel oil.

It is found that crude oil distillate contains light components below diesel, and light components contain gasoline and kerosene, while fuel oil distillate only contains components above diesel[5]. Song Dan [6] set 180 ° C (gasoline distillation range) and 200 ° C (diesel distillation range) as the

limit to distinguish between crude oil and heavy fuel oil, when the initial distillation point of the oil is lower than 180 ° C, it is judged to be crude oil, when the initial distillation point of the oil is higher than 200 ° C, it is judged to be fuel oil.

In general, the initial distillation point of crude oil is lower than that of fuel oil, and fuel oil does not contain components below the initial distillation point of diesel oil. According to the difference of initial distillate point and distillate, crude oil and fuel oil can be distinguished.

2.2.1.2 Density/viscosity method

Density is the most intuitive property index of oil. Viscosity is the basis of international ISO standard classification of fuel oil.

The study found that the density of crude oil and fuel oil will be relatively different, although some crude oil viscosity may be similar to fuel oil[7].

2.2.1.3 Element content identification method

The content of certain elements can be used as an indicator for the identification of crude oil and fuel oil. The content of certain elements in fuel oil is higher than that of crude oil because catalysts containing certain elements are used in the process of processing crude oil into fuel oil through catalytic cracking and hydrocracking processes.

Due to the use of vanadium catalyst in fuel oil production, the content of vanadium in fuel oil is higher than that in crude oil. Under normal circumstances, the content of vanadium in crude oil is low, and even undetectable.[8]

Some studies have determined the silicon and aluminum in crude oil and fuel oil samples by atomic absorption spectrometry, and found that most of the fuel oil contains silicon and aluminum, and crude oil does not contain silicon and aluminum.[6]

2.2.2 Chemical fingerprinting

In practice, the physical properties of crude oil and fuel oil are quite different due to different origins, and it is difficult to accurately distinguish crude oil and fuel oil by measuring a single physical index. Determination of multiple physical indexes can improve the accuracy of identification, but it is time-consuming and costly. In order to achieve rapid and accurate identification, the chemical fingerprint characteristics of crude oil and fuel oil must be analyzed to find subtle differences. Chemical fingerprint identification methods mainly include oil fingerprint, infrared spectroscopy, fluorescence spectrometry, gas chromatography/mass spectrometry and stable isotope mass spectrometry.

2.2.2.1 Oil fingerprint

Oil fingerprints can reflect the original information of oil in the process of production and accumulation, as well as the information of oil processing in the later stage. Oil fingerprint is unique, which lays the foundation for spilled oil identification and oil type identification. Oil fingerprints are usually determined by spectroscopy, chromatography and mass spectrometry.

2.2.2.2 Infrared spectroscopy

Infrared spectroscopy has the advantages of fast analysis speed, low cost, simple operation and non-destructive testing of samples, but it has limited ability to identify similar oil and weathered oil.[9] In recent years, various stoichiometric methods are usually used to process infrared spectral data, which makes the analysis results of oil by infrared spectra more reliable. Wang Li [10] proposed a method of near-infrared spectroscopy combined with principal component cluster analysis to identify spilled oil types. Multivariate scattering correction (MSC) and Norris first-order derivative smoothing pretreatment of near infrared spectra were used to find the principal components, and Ward cluster analysis was used to classify the samples based on the principal components. This method can accurately and quickly classify the spilled oil samples whose volume fraction is between 0.4 and 0.8 mL/L.

Liu Qian [11] established a rapid oil analysis method based on attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), which can be used for the preliminary identification of spilled oil. ATR-FTIR was used to detect 25 kinds of oil products from different sources, the original spectra were preprocessed by mathematical methods such as multivariate scattering correction and continuous wavelet transform, and the spectra were classified by principal component analysis and systematic cluster analysis. The method is effective in distinguishing the oil with large difference of normal alkane, but it still has some limitations in distinguishing the oil with small difference of normal alkane.

2.2.2.3 Fluorescence spectrometry

Fluorescence spectroscopy has the advantages of simple operation, good selectivity, high sensitivity and small sample quantity, but it can only distinguish the oil samples with large differences because it gives less oil fingerprint information. With the development of technology, a variety of fluorescence spectroscopy techniques have emerged, such as three-dimensional fluorescence spectroscopy, synchronous fluorescence spectroscopy, etc., and have been successfully applied in oil detection.

Li [12] successfully distinguished nine different crude oil and diesel samples using fluorescence spectroscopy combined with a principal component analysis algorithm, which was able to further distinguish weathered samples. Yin Xiaonan [13] used three-dimensional fluorescence spectroscopy to distinguish and analyze the common oil samples, studied the weathering change law, established the oil identification methods, and has been successfully applied in many unknown source oil spill accidents. Tian Guangjun [14] used the characteristic parameters of three-dimensional oil fluorescence spectrum to compose the feature vector, and realized the recognition of the characteristic parameters of oil by using neural network technology, which is practical and reliable. Wang Yutian [15] applied principal component analysis (PCA) and BP neural network to oil identification, adopted PCA to pretreat the three-dimensional fluorescence spectrum of mineral oil, selected principal components and applied BP neural network to achieve oil identification, and achieved certain results.

2.2.2.4 Gas chromatography/mass spectrometry

Gas chromatography/mass spectrometry has the advantages of high separation efficiency of gas chromatography and high sensitivity and high selectivity of mass spectrometry. It is one of the most important methods for oil fingerprint analysis and identification at present, and it is also the research focus and hot spot of scholars at home and abroad[16]. Chen Nan [17] used GC/MS to determine the content of 8 typical PAHs in 25 crude oil samples and 26 fuel oil samples as predictive variables. Through multivariate statistical analysis such as principal component analysis, discriminant analysis and Logistic regression analysis, a mathematical model for the classification of crude oil and fuel oil was established. Wang Degao [18] found that the naphthalene/dimethylnaphthalene and naphthalene/monomethylnaphthalene ratios in the diagnostic ratios of PAHs can be used to distinguish between heavy diesel oil and crude oil. Liu Xing [19] quantitatively determined the PAHs content in crude oil and heavy fuel oil from 8 different origin by GC/MS method, and found that the diagnostic ratio (2-m-An /total of MP) could be used for oil identification by comparing the original PAHs spectra, component distribution patterns and characteristic ratios. Zhang

[20] collected 230 crude oil samples and 210 fuel oil samples from all over the world, determined different diagnostic ratios by GC/MS method, proposed 9 oil differential diagnostic ratios based on phenanthrene and anthracene series compounds, and used normal fitting and bar graphs, double coordinate graphs and Bayesian discrimination to verify the accuracy of the newly proposed diagnostic ratios. The recognition rate of Bayes discrimination is 93.92% ~ 99.32%, which can be applied to the actual spilled oil identification.

2.2.2.5 Stable isotope mass spectrometry

Stable isotope mass spectrometry is a method to determine the chemical fingerprint of oil by measuring the stable isotope ratio of carbon, nitrogen, oxygen or hydrogen in each component, which has unique advantages in oil analysis. Ma B ensi [21] used a stable isotope mass spectrometer to distinguish crude oil from fuel oil, using the stable isotopic characteristics of normal alkanes and polycyclic aromatic carbons as variables. Liu Xiaoxing [22] used stable isotope mass spectrometry to determine the carbon stable isotope ratios of n-alkane monomer hydrocarbons in fuel oil and crude oil from three different origins. It was found that the monomer hydrocarbons of fuel oil fluctuated greatly, while crude oil was relatively stable.

2.3 Relevant experimental facilities at home and abroad

2.3.1 Weathering tank of SINTEF Laboratory in Norway

SINTEF has a strong scientific research capability in oil spill emergency response, especially for ice oil spill emergency response, such as ice oil spill drift and weathering trajectory simulation. SINTEF mainly studies the weathering of crude oil, the chemical and physical properties of oil, the emulsification properties, the rheological properties of oil, the weathering of oil in wave tank, the natural change process of oil in the coastline, the chemical properties of crude oil and the properties of sediment, the identification of spilled oil, and the properties of water-soluble oil. The weathering tank used in the above study is 4 meters long, 2 meters wide, 1.5 meters high, 1 meter deep, and 0.5 meters wide circulating channel, as shown in Figure 1.

There is an extended wave making facility at one end of the tank, with a piston boost type wave making facility and a wave breaking plate. The tank is made of stainless steel and consists of different shapes of components (such as elliptical circulation tank, straight channel, etc.). The tank uses air conditioning to control the temperature, and is equipped with water cooling system, which can reduce the water temperature to -2°C . The tank uses a fan to generate air and is equipped with a plastic hose duct, with a maximum wind speed of 10m/s. The tank is equipped with flow making facilities, and the flow rate is 1kn. The tank is equipped with experimental personnel protection facilities. It has a movable artificial beach with a camera system. The experiments carried out in the tank mainly include oil weathering process and mechanism study, long-term weathering and fate study, weathered oil penetration study on different types of coastline sediment layer, and ecological impact study of spilled oil under typical environmental conditions.



Fig. 1 SINTEF enclosed weathering tank

2.3.2 Key Laboratory of Marine Spill Oil Identification and Damage Assessment Technology, SOA (MOIDAT)

MOIDAT has a research laboratory for the environmental behavior of pollutants, including a wave current simulation tank (32 meters long, 0.8 meters wide, 2 meters deep), a longitudinal simulation tank (1.5 meters long, 1.5 meters wide, 4 meters deep), and a weathering simulation tank (3.0 meters long, 2.0 meters wide, 1 meter deep). MOIDAT is the first ministerial-level key laboratory of offshore oil spill established in China, supported by the North Sea Branch of the State Oceanic Administration. MOIDAT carries out research work focusing on spilled oil identification

technology, oil spill environmental behavior process and oil spill ecological environmental damage assessment technology, which serves marine administration and marine environmental protection, and provides scientific basis for China's marine disaster reduction and prevention.

The three main research directions of MOIDAT are oil spill monitoring and identification technology (integrated oil spill monitoring method, spilled oil identification and oil fingerprint database construction technology); ecological and environmental impact of the oil spill (weathering and migration process of the oil spill, biological response mechanism of the oil spill and ecological and environmental impact assessment of the oil spill); and oil spill disposal and ecological restoration technology (oil spill quick disposal technology, marine oil pollution ecological restoration technology).

2.3.3 Summary

It is impossible to distinguish between crude oil and fuel oil by a single method, because of the complexity of the chemical composition and the large number of oil products. In practice, a variety of methods can be combined to improve the accuracy of oil types identification. In practice, after an oil spill accident, the weathering process of the oil will change the fingerprint characteristics of the oil, further aggravating the complexity of oil species identification. The influence of weathering factors should be considered in the identification of oil types.

3. Conclusions

Oil spill composition is complex and difficult to identify. Different methods of oil spill identification have their advantages and disadvantages. It is necessary to combine different identification methods and develop new oil spill identification technology to improve the persuasiveness and reliability of oil spill identification results. Oil spill identification is of guiding significance to the clean-up of oil pollution on the sea, the settlement of liability disputes and the subsequent ecological restoration. Looking forward to the future, it is of great importance to research the following aspects.

3.1 Simulation of controlled environmental conditions for oil spill identification and traceability experiment and simulation of environmental behavior of spilled oil

Analysis of the environmental conditions required for oil spill identification and traceability experimental tank

Put forward the requirements of controllable environmental conditions for oil spill identification and traceability experiment, including but not limited to wave generation, temperature control, wind speed control, flow generation, etc.

3.2 Study on the experimental scheme of oil spill identification and traceability experimental wave tank

According to the requirements of controllable environmental conditions of the oil spill identification and traceability experiment tank, it is necessary to carry out research on the size, scale, shape and material of the oil spill identification and traceability experiment wave tank.

It is necessary to determine the scale of the simulation and the possible application area.

It is necessary to carry out the research on the experimental scheme of wave flume for oil spill identification and traceability experiment.

3.3 Research on experimental procedures for fast detection and accurate traceability based on the combination of wave tank experiment and laboratory analysis

It is necessary to further refine the needs of oil spill identification experiments, and carry out oil spill identification and traceability experiments in the field of marine ecological environment identification and assessment.

It is necessary to establish an oil spill identification and traceability experiment module, and carry out research on oil spill identification technology, oil spill environmental behavior process, and oil spill ecological environmental damage assessment technology, so as to further protect marine environmental protection, and provide more technical support for offshore oil spill monitoring, determination of liability for offshore oil spill and law enforcement.

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5. References

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