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The analysis on trace sulfur compounds in petroleum samples by comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry

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Currently, there are more than 1500 types of organic sulfur compounds in the geologic samples have been identified. The compounds which could express geological information in the field of petroleum exploration are thiophenes, benzothiophenes and dibenzothiophenes they are also often detected in samples of crude oil and source rock. In particular, the alkyl-thiophene compounds could be used to indicate hypersaline environment, and the dibenzothiophene, fluorene and dibenzofuran compounds could be used to analyze palaeosedimentary environment. However, because of the shortage of analytical techniques, the study of application of benzothiophene compounds in petroleum samples is not enough. As we known, the characteristic fragment ions of benzothiophene compounds are m/z 147, 161, 175……, and molecular ions are m/z 148, 162, 176, 190…….. The benzothiophene compounds are always overlapped with some mono-aromatic hydrocarbons, diphenyls and fluorine compounds, and the characteristic ion or molecular ion peaks are often formed co-eluting peaks by using the conventional GC-MS. The peaks of benzothiophene compounds with the lower contents may be affected greatly, or even could not be detected, which will lead to the wrong quantitative results. Comprehensive Two-Dimensional Chromatography with Time-Of-Flight Mass Spectrometry (GC×GC-TOFMS) is a relative new technique for complex compounds analyses. When it is used to detect the benzothiophene compounds in petroleum samples, the GC×GC chromatogram reflects that the second retention times of benzothiophene compounds are higher than those of mono-aromatic hydrocarbons and diphenyl compounds, but lower than those of fluorine compounds due to the polar differences between benzothiophene and other compounds, such as the mono-aromatic hydrocarbons with same boiling points. In this way, the effect of co-eluting peak will be removed and the accurate quantitative results of benzothiophene compounds could be obtained. Moreover, the GC×GC-TOFMS could be used to detect sulfur compounds (especially benzothiophene compounds) existing in petroleum samples, which will achieve accurate quantitative results. This technique could be an effective support for the application of sulfur compounds in the field of petroleum exploration in the near future.

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