

DISCRETE CLASS-TYPE SEPARATION OF THE POLAR AND APOLAR
COMPONENTS OF PETROLEUM

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Identification of the heteroatom (nitrogen, sulphur, and oxygen)-containing compounds of petroleum is of key importance when considering industrial and environmental issues associated with crude oil production. Previously used methods of crude oil fractionation have often proven insufficient in the extent to which they separate oils, not allowing defined ‘molecular’ (class-type) fractions to be obtained. The most commonly reproduced are the so-called SARA (Saturates, Aromatics, Resins, and Asphaltenes) type separations. After the initial SARA separation was introduced (Jewell et al., 1974), significant numbers of modified SARA separations have been developed (e.g. (Hayes and Anderson, 1986, Fan and Buckley, 2002)) utilising a variety of solid phases and techniques, the drawbacks of which are now well known (summarised (Bissada et al., 2016, Kharrat et al., 2007)). Methods able to provide a class-type separation are uncommon and are often extensive, generating large numbers of fractions (e.g. (Snyder and Buell, 1968): 36 fractions). Many normal phase separations result in significant losses due to irreversible adsorption and require asphaltene precipitation prior to separation. Despite the drawbacks, this approach has many benefits, the most significant being the ability to collect fractions based on compound class.

Here we report a new method for the comprehensive separation of crude oils into fractions based on the functionality of the various compound classes. We employed the use of authentic compounds representative of many compound classes known to be present in crude oils. This allowed the creation of an optimised scheme in which class location could be reliably predicted for crude oil separations.

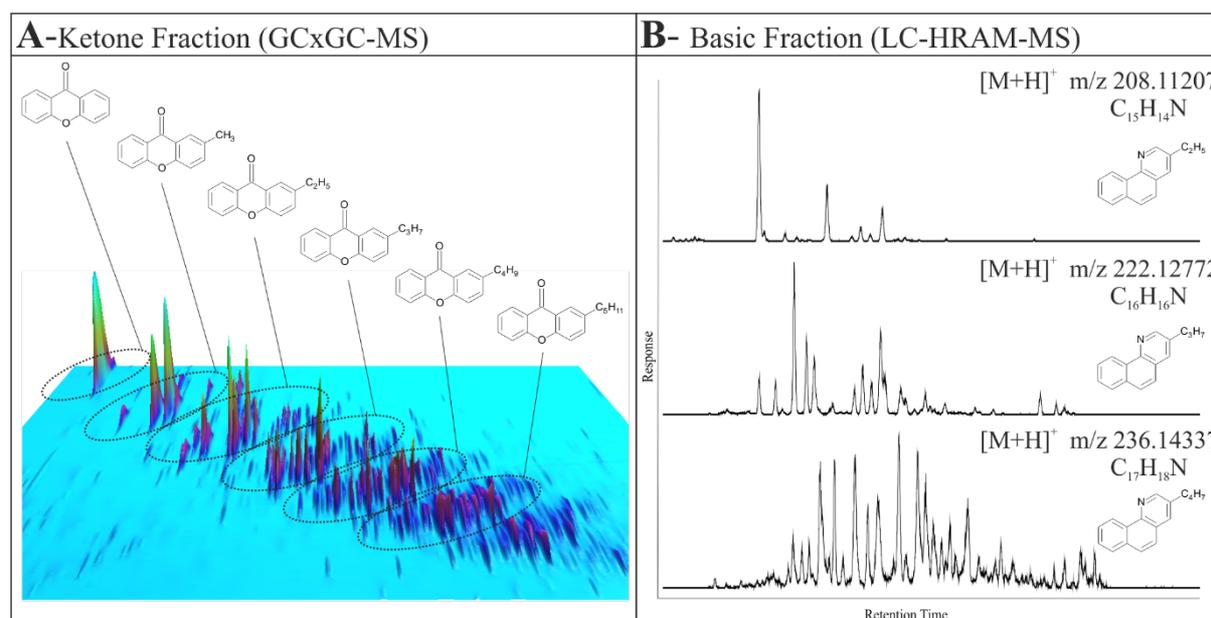


Figure 1- Example data from the analysis of fractions obtained from the separation of Alaska North Slope crude oil. **A-** GC×GC-MS chromatogram of the ketone fraction showing xanthone and the xanthone C₁₋₅ homologs. **B-** LC-HRAM-MS extracted ion chromatograms of homologous series from the analysis of the basic fraction consistent with identification as alkyl benzoquinoline structures (C₁₋₃).

The method utilizes both ion exchange and normal phase chromatography to generate fractions of saturate hydrocarbons, aromatic hydrocarbons, basic compounds, naphthenic acids, ketones, phenols, carbazoles, sulfones, and thiophenes from relatively small samples of crude oil (~0.5g).

Application of the method to five crude oils of varying API gravity (12.1-38.3°) demonstrates its potential for wide-ranging use. Total recoveries from the separation of the five oils were good (77.4-97.5 %) and very good (92.6-102.5 %) once normalised for simple evaporative losses. Separation repeatability was also high, demonstrated by triplicate analyses of model compound mixtures, oils spiked with model compounds and oils alone.

Separation selectivity towards compound classes of interest was further demonstrated by application of the scheme to the Alaska North Slope (ANS) crude oil and analysis of fractions. Excellent separation by comprehensive two dimensional gas-chromatography mass-spectrometry (GC×GC-MS) of discrete fractions of carbazoles, dibenzothiophenes, fluorenones and xanthenes (Figure 1A) allowed easy identification of individual parent and C₁₋₅ alkyl homologs. Analysis of fractions by GC×GC-MS also allowed a series of thioxanones to be identified within crude oils for the first time.

Analysis of cationic fractions by liquid chromatography high-resolution accurate mass-mass spectrometry (LC/HRAM-MS) has revealed a series of highly complex mixtures. Mass spectral ions primarily presented with even masses (indicative of an odd number of N and present as protonated species), high ring double bond equivalency and occurred within the mass range *m/z* 150-1400. LC separation allowed the separation of structural isomers (Figure 1B) and some of the lower molecular weight aromatic nitrogen structures can be identified by comparison with model compounds.

References

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