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RAPID AND EFFICIENT PROTOCOL FOR THE SEMI-QUANTITATIVE ANALYSIS OF C_{2+} CARBOXYLIC ACIDS IN CRUDE OILS

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A wide range of carboxylic acids has been detected in minor to moderate amounts in many oils. Detected species include alkanoic acids (Rodrigues et al., 2000), naphthenic acids (Aitken et al., 2004) and hopanoic acids (Pan et al., 2006). These compounds are not routinely analysed due to laborious workup procedures, often with low or inaccurate recoveries. The methods often require large amounts of solvent which prevents the analysis of low molecular weigh carboxylic acids due to evaporative losses during sample preparation.

Here we present an alternative method for the analysis of carboxylic acids from crude oils. The protocol is based on small-scale column (Pasteur-pipette) liquid chromatography and allows the rapid throughput of large sample sets. After eluting hydrocarbons and heterocycles with apolar and aromatic solvents, a polar acidic fraction is recovered with diethyl ether (2% formic acid). Following the butylation of this fraction, non-carboxyl interferences are removed on a silica column.

Recoveries are substantially higher than previously published methods (up to 100%) and are reproducible and consistent, thus allowing for accurate quantification.

To prevent the loss of low molecular weight carboxylic acids, the method uses a minimum amount of solvent and the recovered acids are derivatised to *n*-butyl esters. In this manner compounds as volatile as acetic acid ($C_{2:0}$) can be quantitatively measured when using corresponding deuterated surrogate standards. In addition, multifunctional acids and long-chain alkanoic acids are also semi-quantitatively recovered in the same fraction.

Test trials revealed the optimum conditions for the Fischer esterification reaction (time, temperature, reagents) using sulphuric acid (H_2SO_4) and boron trifluoride (BF_3) as catalysts. The use of H_2SO_4 has a number of advantages over BF_3, since the latter reagent has a limited shelf-life, forms a health hazard and can lead to artefacts during the workup procedure.

We will present a clear depiction of the described method in an attempt to encourage the analysis of carboxylic acids which should lead to an increased understanding of the origin and fate of this compound class in petroleum.

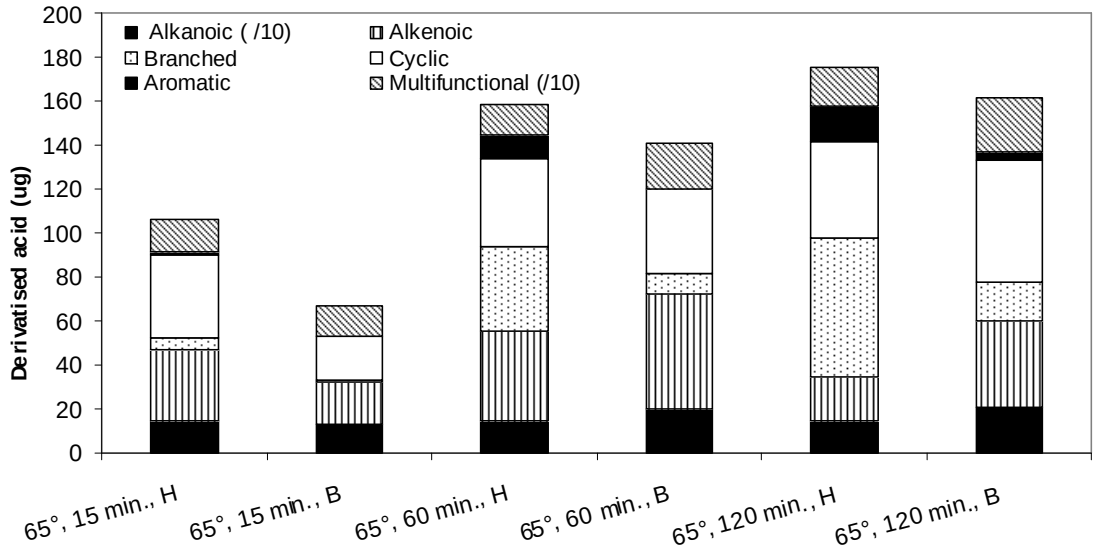

Figure 1. Compared butylation efficiency using 100ul n-butanol. Time and temperature conditions, respectively catalyst (B- BF_3; H- H_2SO_4) are listed on the x-axis. Note the greater derivatisation efficiency when using H_2SO_4, which is particularly pronounced in aromatic and branched acids.

REFERENCES

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