

Determination of wax content of crude oils using TLC-FID

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The presence of wax in crude oils may have negative effect on their properties and handling. One problem in dealing with wax is the complex nature of the wax as well as lack of clear understanding and definition of wax in crude oils [1, 2]. The complexity is further illustrated by the lack of a fundamental or standard method for wax determination in crude oils. This paper introduces a new method for the determination of wax content of crude oils. The method is based on thin layer chromatography with flame ionization detection (TLC-FID, known as latroscan technique) [3].

The principle of the test method is shown in Fig. 1. First, 1 μ l of sample solution (1% w/v prepared in chloroform) is spotted near the bottom of a Chromarod. After evaporation of the solvent at ambient condition, the rod in a frame is placed in a lined chamber containing *n*-heptane and developed for 35 min. By this step, a fraction of saturates is separated from other more polar components based on good solubility of saturates in *n*-heptane and weak strength of interaction with an adsorbent (silica). After drying, the rod is turned upside down, and hung and conditioned inside the second chamber containing methyl-ethyl ketone (MEK) at low temperature (typically -20°C). The waxes that are insoluble in the cold MEK are separated from other saturated compounds. The separated fractions are quantified with FID.

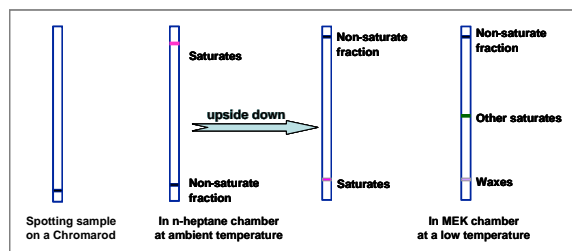


Fig. 1. Illustration of separation of waxes by TLC

The test method has been verified using various model compounds, including *n*-alkanes, isoalkanes, and synthetic waxes. It was found that the waxes detected by this method are mainly composed of *n*-alkanes ranging from C20 to C40, as well as large isoalkanes and cycloalkanes that are soluble in *n*-heptane.

A typical example of TLC-FID chromatogram for a crude oil after the first step development by *n*-heptane and the second step development by MEK at -20°C is

shown in Fig. 2. The results obtained for a number of crude oils are shown in Table 1, along with the measurements made by differential scanning calorimetry (DSC).

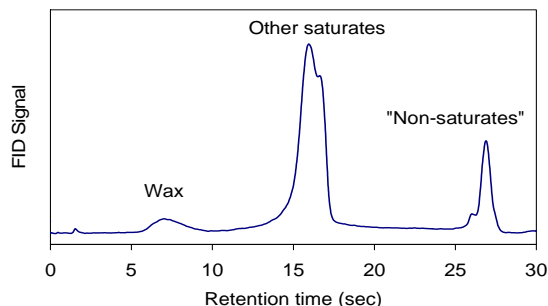


Fig. 2. Wax determination of a crude oil by TLC-FID

Table 1. Wax content (%) determined by TLC-FID and DSC

Oil samples	TLC-FID	DSC
North Sea	0.1	0.0
Russian I	1.9	12.2
Russian II	5.1	9.4
Venezuelan I	0.0	0.0
Venezuelan II	0.6	4.1

In general, the wax contents measured by TLC-FID at -20°C are lower than those by DSC. The difference is due to the fact that small and large crystallizing molecules are not detected as the waxes by TLC-FID at the selected temperature. This was further confirmed by high temperature gas chromatography (HTGC). A series of experiments on effect of temperature indicated that the determined wax contents increase with decreasing MEK temperature in TLC. The observation is interesting, as it suggests a possibility to characterize waxes of a certain molecular weight range only by changing the temperature of elute.

It has been demonstrated that the new test method is quick, simple, and easy to run. In addition to application to crude oil samples, it is applicable to other petroleum materials, such as refining residue, and bitumen or asphalt binder.

References

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- [3] Lu, X., et al. (2008) Fuel. 87, 1543-1551.