



# RESEARCH

## A New Method for the Determination of Wax Content of Crude Oils

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A new method has been developed for determining the wax content in crude oils. Saturate fractions, obtained during hydrocarbon group separations by open column chromatography, were analyzed by gas chromatography with flame ionization detection (GC/FID). The ratio of the resolved  $C_{18}+$  area to the total area was used to calculate the wax content of the oil.

Using both the new method and the conventional method (gravimetric determination of solvent-precipitated waxes) 25 crude oils were analyzed. Overall, very good agreement was found between the two methods.

One solvent-precipitated wax sample was subjected to a clean-up procedure and *n*-alkane distributions were obtained for the 'clean' and 'dirty' waxes. Co-precipitation of polar compounds and entrapment of oil during wax crystallization can cause the gravimetric wax contents of some oils to be exaggerated. It is suggested that the most problematic oils are those that exhibit non-Newtonian flow behaviour at 15°C.

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**Keywords:** Petroleum waxes, coprecipitation, simulated distillation.

### Introduction

Petroleum waxes are of two general types: paraffin or macrocrystalline waxes, composed primarily of straight-chain saturated hydrocarbons with 18-36 carbon atoms, and microcrystalline waxes that contain a large percentage of branched and cyclic hydrocarbons with carbon numbers in the 30 to 60 range (Mansoori, 1996).

In the environment, the effects of weathering and low ambient temperatures produce dramatic changes in the rheological properties of even moderately waxy crude oils. This in turn, significantly affects other oil properties, such as evaporation and dispersibility. Hence, accurate determination of the wax content of crude oils is important.

The most common method for the determination of waxes in crude oils is precipitation from cold solvent mixtures, with gravimetric determination of the recovered waxes. However, the co-precipitation of polar material with the waxes and the trapping of lighter hydrocarbon components tend to exaggerate wax content, especially with heavier oils (Ronningsen & Bjorndal, 1991).

This paper describes a new method for determining the wax content in crude oils, using saturate fractions collected from hydrocarbon group separations.

### Methods

#### *Determination of wax content—gravimetric method*

Details of this method have been described previously (Jokuty *et al.*, 1994). Asphaltenes are

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removed from the crude oil by precipitation from *n*-pentane. Waxes are precipitated from the deasphalted oil (maltenes) with a methylene chloride/methylethyl ketone mixture at  $-30^{\circ}\text{C}$ , filtered, dried and weighed.

#### Determination of wax content—gas chromatographic method

The saturate fraction of a crude oil is obtained by hydrocarbon group separation, described briefly as follows. After removal of asphaltenes by precipitation from *n*-pentane, the maltenes are separated on an open silica column into saturates, aromatics and resins by sequential elution with hexane, hexane/benzene, methanol and methylene chloride (Jokuty *et al.*, 1995).

It is assumed that resin and asphaltene contents are not affected by evaporative losses, and that the aromatic portion of the light ends lost during solvent recovery can be equated to the benzene, toluene, ethylbenzene, xylenes and  $\text{C}_3$ -substituted benzenes (BTEX +  $\text{C}_3$ -benzenes) content of the crude oil (Wang *et al.*, 1995). The remainder of the light ends, calculated by difference, is referred to as the low boiling saturates (LBS). The saturates recovered from the column are referred to as the high boiling saturates (HBS). The HBS sample is prepared and run as for simulated distillation (SIMDIS) (Jokuty *et al.*, 1996). The SIMDIS analyzer uses a special high-temperature column and is capable of resolving *n*-alkanes from  $\text{C}_5$  to  $\text{C}_{120}$ .

The chromatogram obtained is integrated once to obtain the total area, and a second time to obtain the area of the resolved peaks, beginning at a retention time corresponding to that of *n*-octadecane (*n*- $\text{C}_{18}$ ), as determined from the analysis of a calibration mixture.

To calculate the wax content of an oil, first the HBS content is calculated:

$$\text{HBS\%} = 100 \times \frac{\text{HBS recovered}}{\text{maltenes used}} \times \frac{\text{maltenes recovered}}{\text{oil used}} \times \frac{(\text{saturates} + \text{aromatics})_{\text{expected}}}{(\text{saturates} + \text{aromatics})_{\text{recovered}}}$$

The wax content is calculated by multiplying the HBS percent by the ratio of the area of the resolved  $\text{C}_{18}$  + portion of the chromatogram to the total area.

#### Wax clean-up method

This method was based on a procedure described by Ronningsen & Bjorndal (1991). A Sumatran light wax sample was dissolved in hexane. This solution was filtered through a small amount of silica. The hexane was evaporated and the cleaned wax air-dried overnight and weighed.

#### GC/FID and GC/MS analysis of saturate fractions and waxes

Saturate samples were weighed and dissolved in hexane. Wax samples were weighed and dissolved in toluene. *N*-alkane distributions, from  $\text{C}_8$  to  $\text{C}_{41}$  were determined by GC/FID and GC/MS analyses as described in Wang *et al.* (1994).

## Results

Both the gravimetric method and the GC method were used to determine the wax contents of 25 crude oils. The range of GC wax values was 1–24%. The range of gravimetric wax values was 1–37%. Delta values, the difference between the two wax contents, ranged from  $-17$  to  $+2$ , with 80% falling between  $-2$  and  $+2$ , inclusive. The results for a representative selection of this majority group are presented in Table 1. Table 2 presents the wax results for the five oils with large delta values, together with other relevant properties.

A solvent-precipitated wax sample from Sumatran light crude oil was subjected to the clean-up procedure described above. A summary of the alkane distributions for the 'clean' and the 'dirty' wax are presented in Table 3.

## Discussion

Overall, the results from the new method compare very well with those from the old gravimetric method. Twenty of the 25 oils tested showed excellent agreement (delta between  $-2$  and  $+2$ ) between their two wax contents. Of the remaining five oils, two (Rangely and Malongo) had wax contents that were in good agreement with delta values of  $-5$  and  $-3$ , respectively. Three oils (Taching, Sumatran light, and Sumatran heavy) had GC wax contents much lower than gravimetric wax contents, with delta values of

Table 1 Wax contents of selected crude oils

Oil name	GC waxes (wt%)	Gravimetric waxes (wt%)	Delta*
Gulfaks	4	2	2
Arabian light	6	4	2
Iranian heavy	6	4	2
Louisiana	4	3	1
Federated	7	6	1
Arabian medium	7	6	1
Oseberg	5	5	0
Point Arguello light	7	7	0
Brent	8	8	0
Statfjord	8	8	0
IFO 180	7	8	-1
Hondo	4	6	-2

\*Delta = GC wax - Gravimetric wax.

**Table-2** Wax contents and other properties of selected crude oils

Oil name	Malongo	Rangely	Taching	Sumatran light	Sumatran heavy
GC waxes (wt%)	11	9	24	24	7
Gravimetric waxes (wt%)	14	14	33	37	24
Delta*	-3	-5	-9	-13	-17
Density@15°C (g ml <sup>-1</sup> )	0.8701	0.8567	0.8700	0.8600	0.9312
Viscosity@15°C (mPa·s)	63	33	5,138,000**	322,800***	117,500***
Pour point (°C)	21	17	38	38	18
Low boiling saturates (wt%)	13	17	0	8	0
High boiling saturates (wt%)	49	54	74	62	46
Resins (wt%)	9	5	9	6	13

\*Delta = GC wax - Gravimetric wax.

\*\*Shear rate = 0.1 s<sup>-1</sup>.

\*\*\*Shear rate = 1 s<sup>-1</sup>.

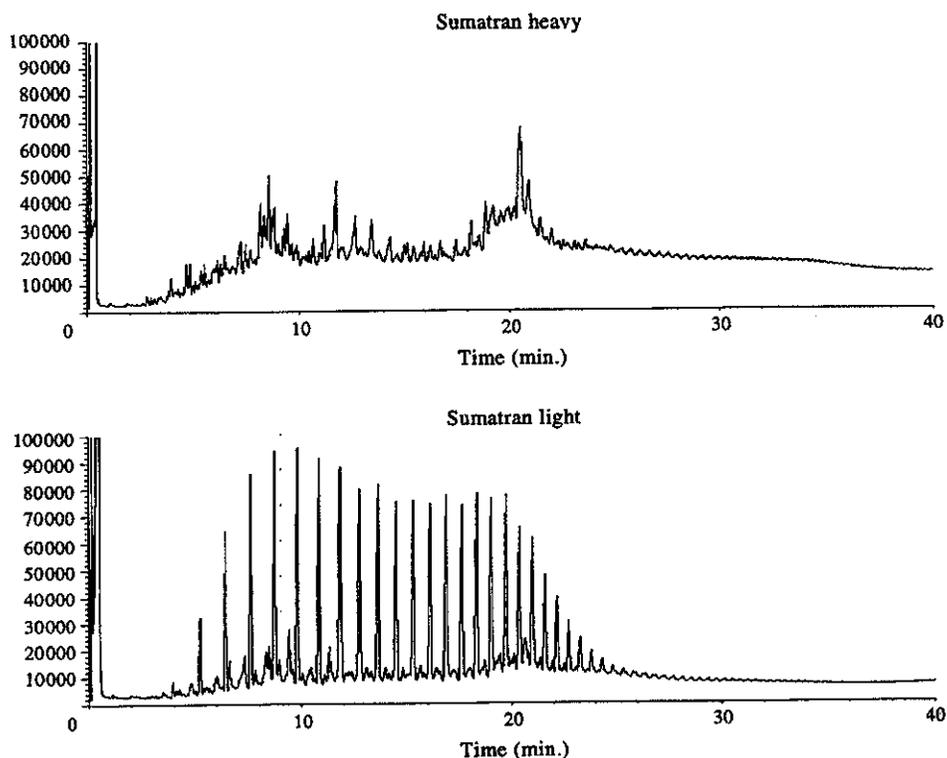
**Table 3** Summary of *n*-alkane distributions

<i>n</i> -Alkanes (mg g <sup>-1</sup> )	Sumatran light dirty wax	Sumatran light clean wax
Total	368	497
% < C <sub>18</sub>	5%	1%
% C <sub>18</sub> +	95%	99%

-9, -13, and -17, respectively. To understand why the GC and gravimetric wax contents differ so much for these three oils, it is helpful to look at some of their

other chemical and physical properties as summarized in Table 2.

Sumatran light and Taching are very waxy oils, as is evident from their very high pour points. As shown in Table 3, in the Sumatran light wax samples, alkanes lighter than C<sub>18</sub> accounted for 5% of the total *n*-alkanes found in the 'dirty' wax, but only 1% in the 'clean' wax. Also, cleaning the wax resulted in a 35% increase in the *n*-alkane content, from 368 mg g<sup>-1</sup> to 497 mg g<sup>-1</sup>, indicating the removal of non-alkane material. Low boiling saturates are absent in Taching. In view of this evidence, the delta value of -9 for Taching is probably due solely to co-precipitation of



**Fig. 1** Chromatograms of Sumatran heavy and Sumatran light saturate fractions.

resins (9%), while the delta value of  $-13$  for Sumatran light is likely due to a combination of co-precipitation of resins (6%) and entrapment of oil during wax crystallization.

Figure 1 shows the extreme difference in the amount of resolved material in the saturate fractions of Sumatran heavy and Sumatran light. Clearly, Sumatran heavy is much less waxy than Sumatran light. This is confirmed by a much lower pour point for Sumatran heavy. Taking into account that the total saturate content of Sumatran heavy is low compared with Sumatran light, that low boiling saturates are absent in the former oil, and that the resin content of Sumatran heavy is more than twice that of Sumatran light, it is probable that the delta value of  $-17$  for Sumatran heavy is due primarily to co-precipitation of resins and entrapment of oil during wax crystallization.

## Conclusions

For most oils, the GC wax content and the gravimetric wax content are comparable. The gravimetric method will generally produce an acceptable result. However, for some oils, notably those with non-Newtonian flow behaviour at  $15^{\circ}\text{C}$ , the GC method gives a more accurate value. This could be an important consideration when determining wax contents of weathered crude oils, as many oils exhibit non-Newtonian flow behaviour after moderate evaporative losses. The GC method also offers a

considerable reduction in time, effort and cost to produce wax content data.

**Acknowledgements**—This work was co-funded by the United States Minerals Management Service and the Emergencies Science Division of Environment Canada.

## References

- Jokuty, P., Whiticar, S. and Fingas, M. (1994) Oil analytical techniques for environmental purposes. In *Proceedings of the 17th Arctic and Marine Oil Spill Program Technical Seminar*, pp. 245–260. Environment Canada, Ottawa, Ontario.
- Jokuty, P., Whiticar, S., Fingas, M., Meyer, E. and Knobel, C. (1995) Hydrocarbon groups and their relationships to oil properties and behaviour. In *Proceedings of the 18th Arctic and Marine Oil Spill Program Technical Seminar*, pp. 1–19. Environment Canada, Ottawa, Ontario.
- Jokuty, P., Whiticar, S., Wang, Z., Fingas, M., Lambert, P., Fieldhouse, B. and Mullin, J. (1996) In *A Catalogue of Crude Oil and Oil Product Properties*, Manuscript Report EE-157, pp. A6–A7. Environment Canada, Ottawa, Ontario.
- Mansoori, G. A. (1996) Wax and waxy crude oil. The role of temperature on heavy organics deposition from petroleum fluids. [Http://www.uic.edu/~mansoori/Wax.and.Waxy.Crude\\_Html](http://www.uic.edu/~mansoori/Wax.and.Waxy.Crude_Html), University of Illinois, Chicago.
- Ronningsen, H. P. and Bjorndal, B. (1991) Wax precipitation from North Sea crude oils. 1. Crystallization and dissolution temperatures, and Newtonian and non-Newtonian flow properties. *Energy and Fuels* 5(6), 895–908.
- Wang, Z., Fingas, M., Landriault, M., Sigouin, L. and Xu, N. (1995) Identification of alkyl benzenes and direct determination of BTEX and (BTEX + C<sub>3</sub>-benzenes) in oils by GC/MS. In *Proceedings of the 18th Arctic and Marine Oil Spill Program Technical Seminar*, pp. 141–164. Environment Canada, Ottawa, Ontario.
- Wang, Z., Fingas, M. and Li, K. (1994) Fractionation of a light crude oil and identification and quantitation of aliphatic, aromatic, and biomarker compounds by GC-FID and GC-MS, part I. *J. Chrom. Sci.* 32, 361–382.