

AN IMPROVED TITRATION METHOD FOR DETERMINATION OF ACID AND PHENOL CONTENT IN CRUDE OILS COMPARED TO EXTRACTION AND HPLC CHARACTERISATION

Tanja BARTH and Morten STRAND

Department of Chemistry, University of Bergen, Allegaten 41, N-5007 Bergen, Norway

The standard method for determining the total amount of acidic compounds in crude oils is by non-aqueous titration with potassium hydroxide, and gives a total acid number – TAN – which is intended to be a measure of all acidic functions in the sample (ASTM D-644-81, 1987). This procedure accurately determines the concentration of carboxylic acids and compounds of equivalent acidity in the sample. However, phenolic compounds and other weaker acids are not within the range of acidities covered by the method. The TAN determination thus gives no information about a considerable part of the compounds that in other contexts are included in the acid fraction, and which may be important for many physical properties of the oils, e.g. surface activity in mineral-oil-water interactions, emulsion stability and corrosion risk.

The range of compounds determined by non-aqueous titration is a function of the solvent system and strength of the base. Using an alternative solvent system, we have developed a procedure that determines the concentration of compounds both in the carboxylic acid pK_a range (TAN-C) and in the phenolic pK_a range (TAN-P) in crude oils in a single titration. The results show that the concentration of the titrable phenolic compounds is comparable to the stronger acid content for biodegraded oils with high TAN values, and significantly higher in low TAN oils, see Figure 1.

Data presenting the scope of the improved TAN determination will be presented, and compared to the results from ion exchange based extraction of acids and HPLC determination of the acid composition using a recently developed procedure that separates the acids into fractions based on acid strength (Borgund *et al.*, 2007). The differences in distribution of the acids in biodegraded and non-biodegraded oils will be focussed.

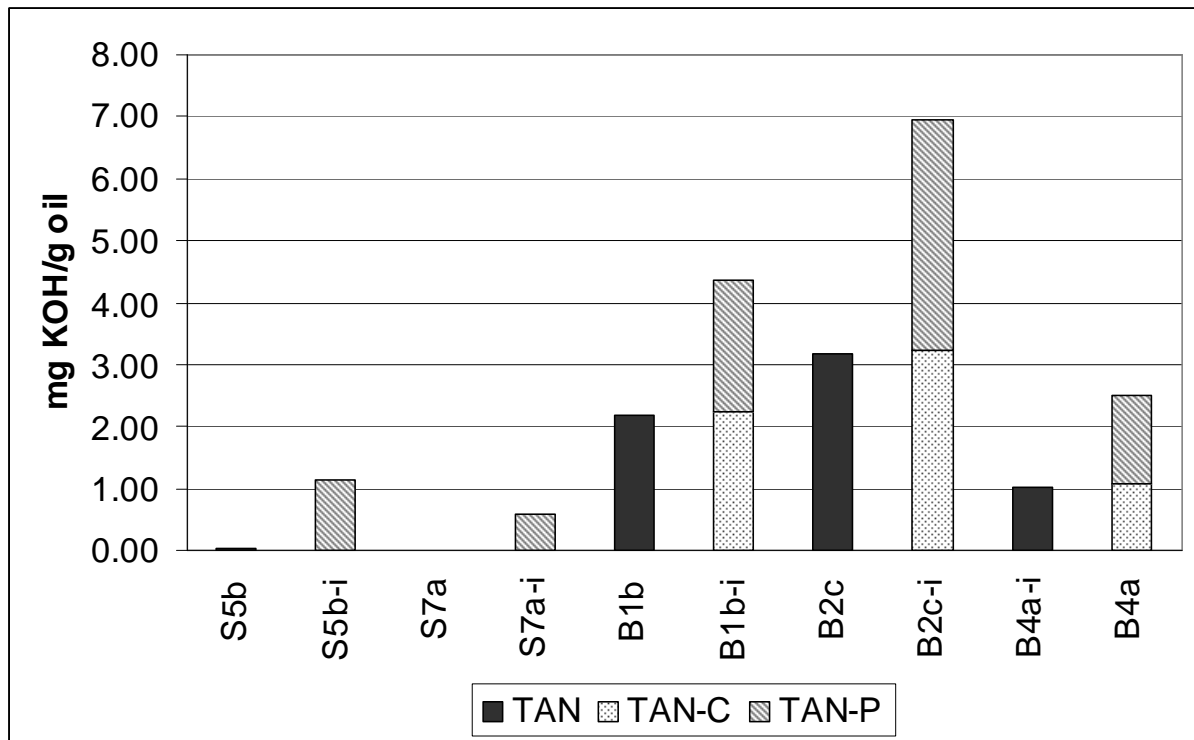


Figure 1. TAN by conventional titration compared to TAN-C and TAN-P values for 5 North Sea Crude oils. Oils S5 and S7 are non-biodegraded and oils B1, B2 and B4 are biodegraded. The results labelled “i” are from the improved titration method.

REFERENCES

- ASTM D-644-81 (1987) Standard test method for neutralisation number by potentiometric titration.
- Borgund Anna E., Erstad K. and Barth, T. (2007) Normal phase High Performance Liquid Chromatography for fractionation of organic acid mixtures extracted from crude oils. Submitted, Journal of Chromatography.