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Naphthenic Acid Analysis
TAN – NAN – NAT- MS

By
Saadedine Tebbal, Ph.D.
SET Laboratories, Inc.

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One-Stop Materials & Corrosion Resource

Introduction

- **Refiners use TAN values extensively for calculations of acid discount and to predict the corrosivity of a stream. They have rules based on TAN limiting their choice of crude oils to be processed.**
- **The TAN per ASTM D664 was developed initially in 1964:**
  - **Section 1.2 - "indicate relative changes that occurs in oil during use under oxidizing condition for lubricants and refined products".**
  - **Section 5.1 - "is used as a guide in the quality control of lubricating oil formulations"**
  - **Section 5.2 – "No general correlation is known between acid number and the corrosive tendency of oils toward metals"**

TAN per ASTM D664

TAN analysis is a potentiometric titration in non-aqueous solution. It is more an art than science.

- **Short-term life of electrodes because they are used in non-aqueous media. They need cleaning and hydration after each titration. The reference electrode junction clog easily. Potential between two buffer solutions need to be checked daily.**
- **The oil needs to be dissolved in a special solvent mixture which contains enough water so that the pH electrode can measure a potential .**
- **Need for a blank determination regularly**
- **End point is not obvious and depend on the buffers used and the set-up of the automatic titrator for volume dispensing and end-point calculations.**
- **No available standard. If available, need to be stable with time.**
- **TAN of 1→ Repeatability = 0.08, Reproducibility = 0.28**

Glossary

- **TAN – Total acid number per ASTM D664**
- **NAN – Naphthenic acid number from extraction by chromatography, then analysis by FTIR. The wt% obtained is then converted to an acid number assuming a MW of 250 for whole crude and 300 for cuts.**
- **NAT – Total acid number per ASTM D664 after extraction of the acids from the oil by chromatography.**
- **MS – Mass spectroscopy using extracted sample to yield average molecular weight (used to get an exact NAN) naphthenic acid distribution and prediction of acid distribution of blends from that of crude slates.**

Outline

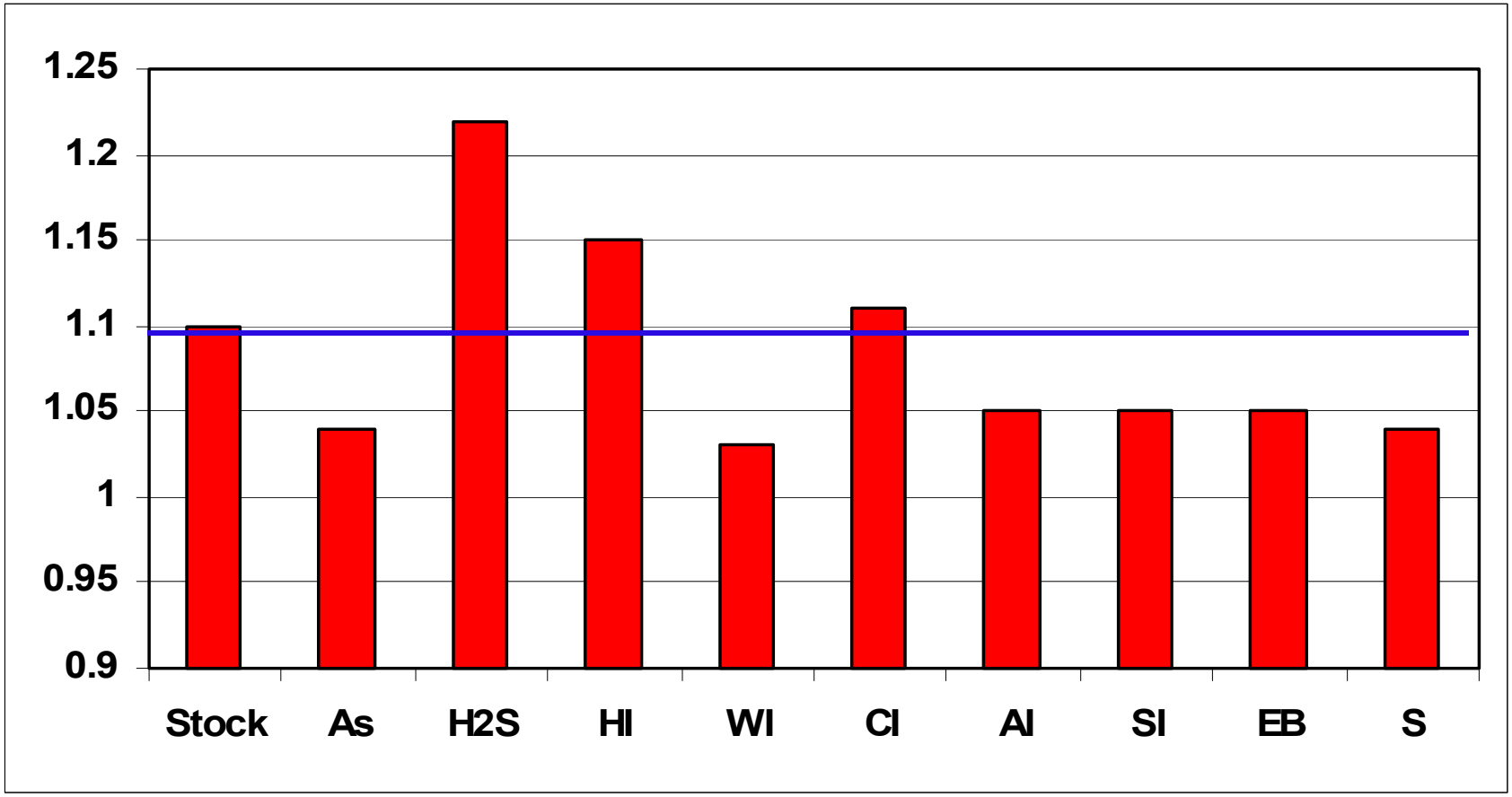
- Effect of oilfield chemicals on TAN.
- Analysis for TAN, and NAN of solutions of 1 wt% nap acids in mineral oil.
- Effect of calibrating acid on NAN.
- Comparison of TAN and NAN of several crude oils.
- Effect of average molecular weight on NAN determination.
- MS use in predicting blends properties
- Conclusions

Effect of Additives on TAN (1)

The effects of the following additives on the TAN of a stock solution of 4 g/L of Fluka nap acid in LVT 200 (TAN = 1.10, NAN = 0.82, NAT = 1.10)were measured:

- **Demulsifier (EB)– 100 ppm**
- **Scale inhibitor (SI)– 100 ppm**
- **Corrosion Inhibitor (CI)– 500 ppm**
- **Wax inhibitor (WI) – 500 ppm**
- **Asphaltene inhibitor (AI)– 1000 ppm**
- **Hydrate inhibitor (HI)– 1000 ppm**
- **Asphaltene (As)– 10%**
- **Elemental sulfur (S)– 100 ppm**
- **H_2S (H2S)– 30 min bubbling**

Effect of Additives on TAN (2)



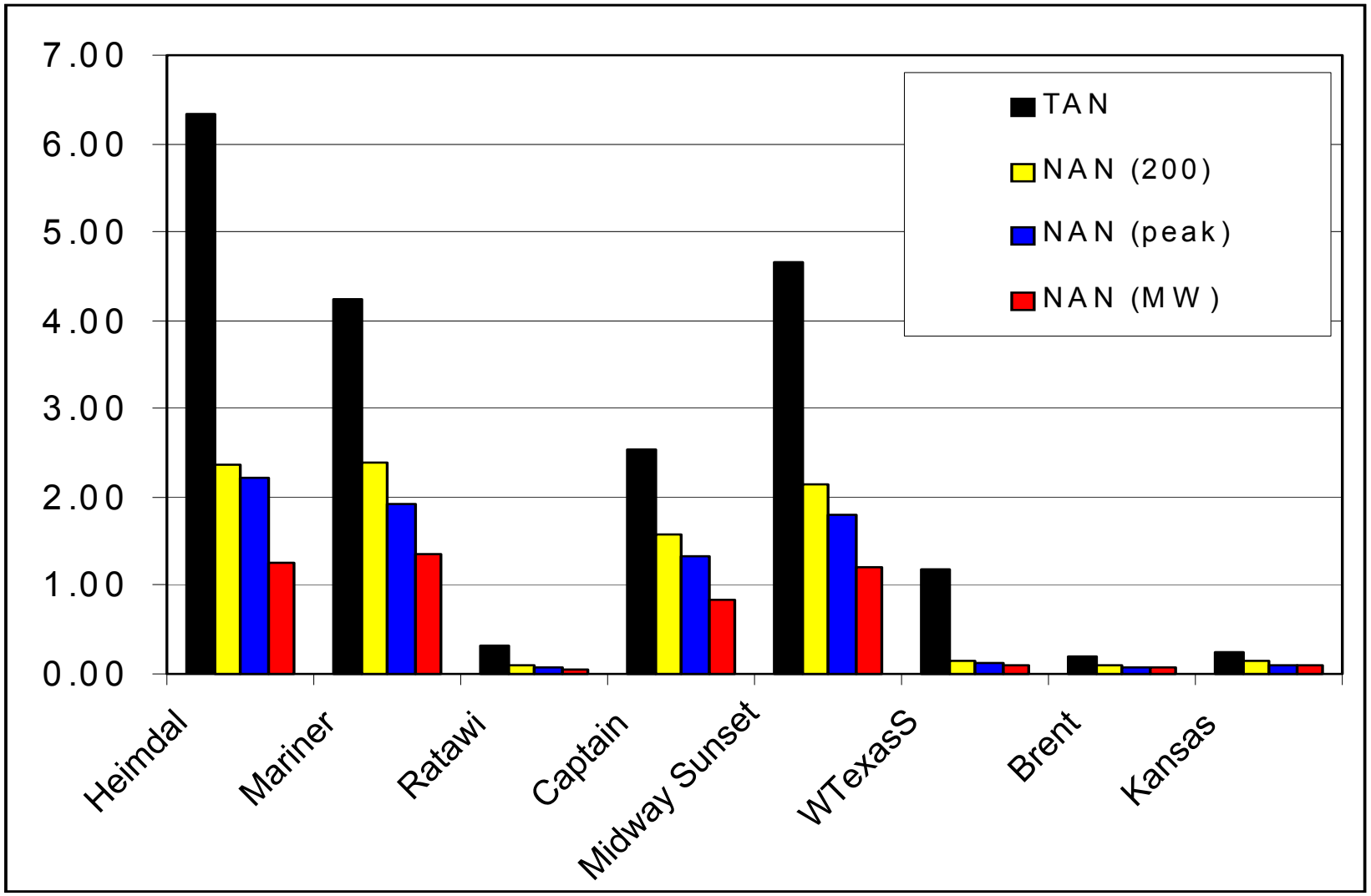
Naphthenic Acids Analysis

Analysis for TAN, NAN of 1% wt of the following naphthenic acids in LVT200 mineral oil:

- **Fluka – TAN of 230**
- **Merichem BW 5810 – TAN of 216**
- **Merichem BW 5811 – TAN of 234**

Acid	TAN	NAN (Same Acid)	NAN (Fluka)	NAN (BW5810)	NAN (BW5811)
Fluka	2.90	2.51	2.51	2.49	1.82
BW 5810	3.07	3.02	3.16	3.02	2.73
BW 5811	2.80	2.63	3.18	3.07	2.63

Effect of Average MW on NAN



TAN-NAN of 6 Crude Oils

Crude Oil	TAN	NAN
1	0.79	0.47
2	0.79	0.43
3	0.47	0.28
4	2.18	1.04
5	0.77	0.42
6	1.84	1.33

MS - Prediction of Blends (1)

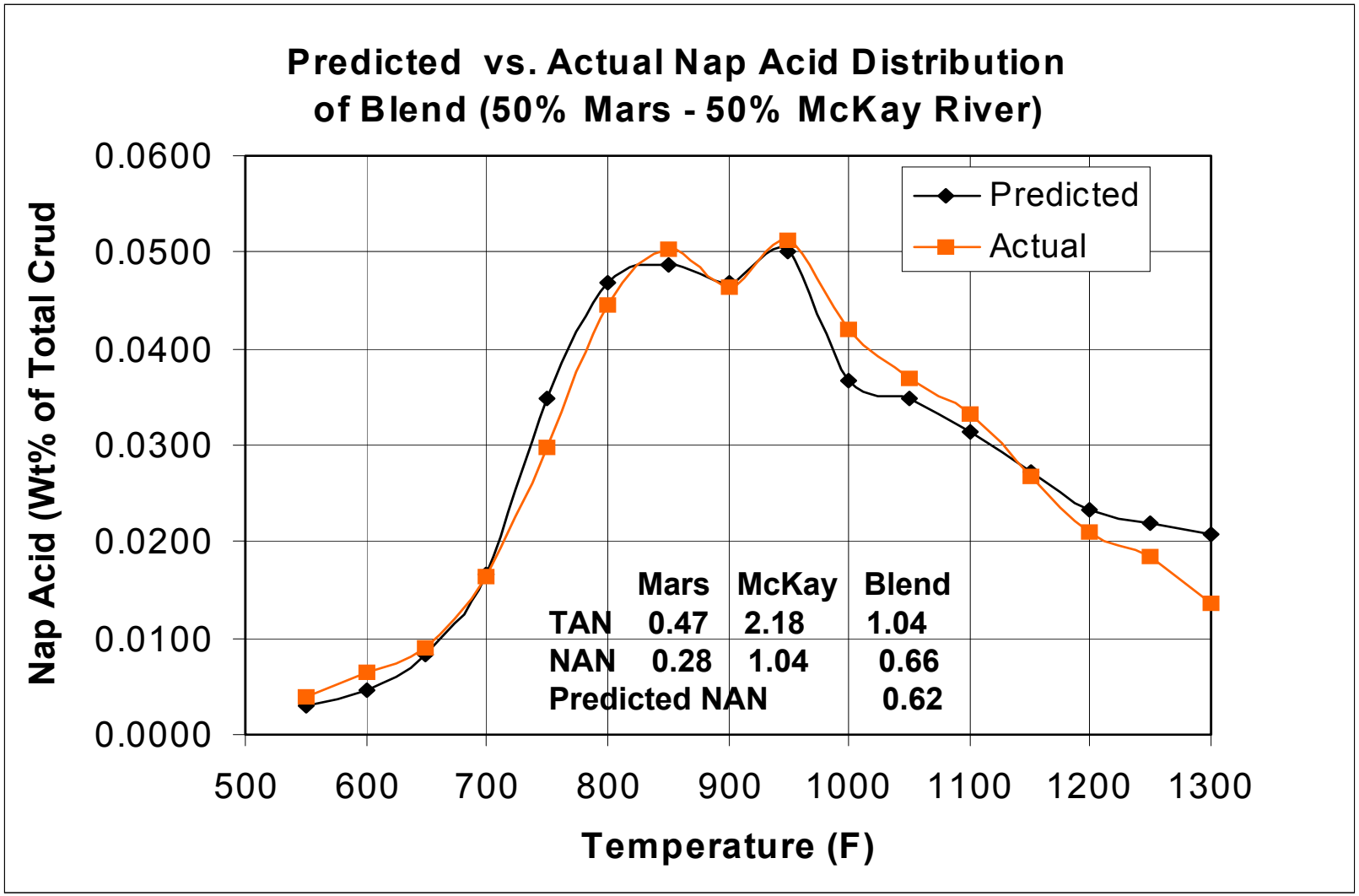
Starting from the MS of each crude slate comprising the blend, the following can be predicted for the blend and its cuts :

- **Average MW of nap acids**
- **Weight percent of nap acid**
- **NAN**
- **Nap acid distribution for the blend**

The following are needed:

- **Composition of the blend (% of each crude slate)**
- **Cut point temperature range**
- **Yield of cuts**

MS - Prediction for Blends (2)



Conclusions

- TAN and NAN – Need for a stable naphthenic acid standard to calibrate titration unit and FTIR
- NAN values generally lower than TAN especially when the right Molecular Weight is used.
- MS essential in determining exact NAN.
- MS can predict properties of blends and cuts.
- Other easier analytical methods that might replace TAN, NAN, NAT analysis
  - Catalysed thermometric titration (thermocouple)
  - British Petroleum Institute new method IP400 that uses conductometric titration.

Thank You

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Any Questions ?