Acid Number Measurements Revisited

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PRRC/ New Mexico Tech

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Outline

- Brief introduction to AN.
- Revised AN measurement.
- AN results from revised techniques.
- Correlation of AN with oil properties.
- Summary

Why do we measure AN?

AN is an important oil property that impacts:

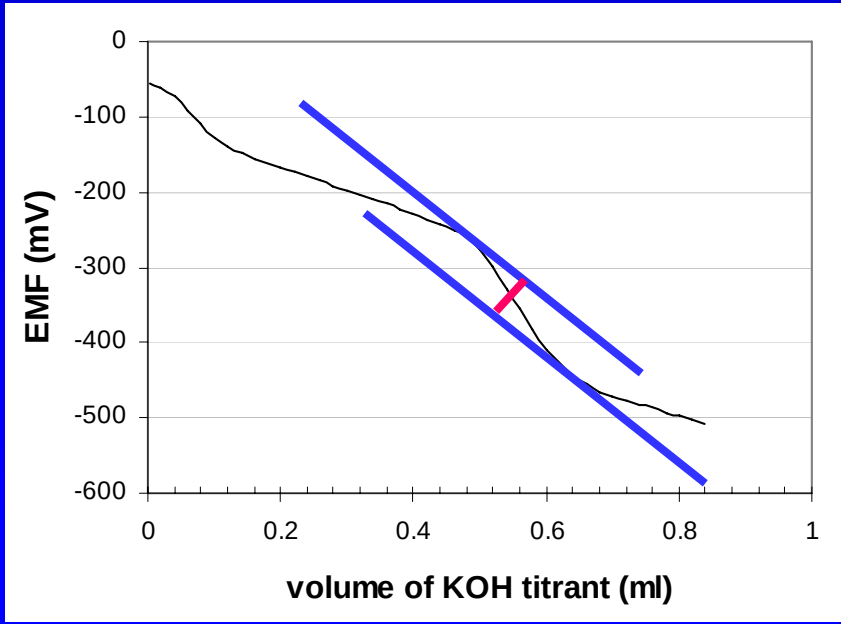
- Efficiency of alkaline/surfactant flooding
- Corrosion of refinery facilities
- Correlation with interfacial properties

Limitations of the ASTM method

- Requires a large quantity of oil (~20g)
- Titration end point can be difficult to detect
- Values measured in different labs are not always comparable.

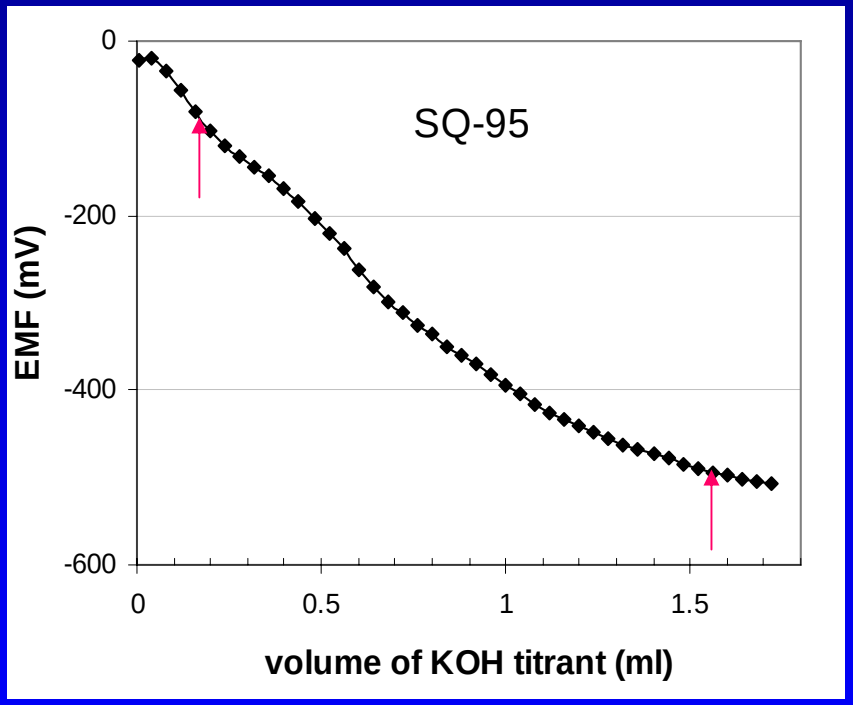
ASTM Method D664-01

- Non-aqueous potentiometric titration.
- About 20g oil are dissolved in an alcoholic solvent mixture (50% toluene, 49.5% IPA, and 0.5% water)
- KOH is used as titrant and AN is defined in mg KOH/g oil.

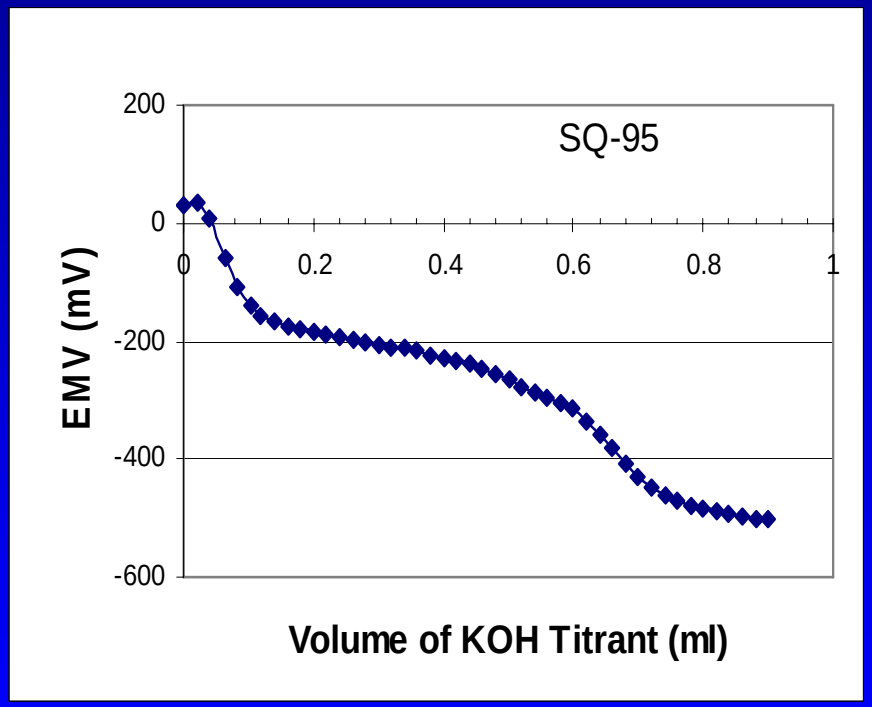


Titration Curves with D-664 Method

Without stearic acid spike



With stearic acid spike



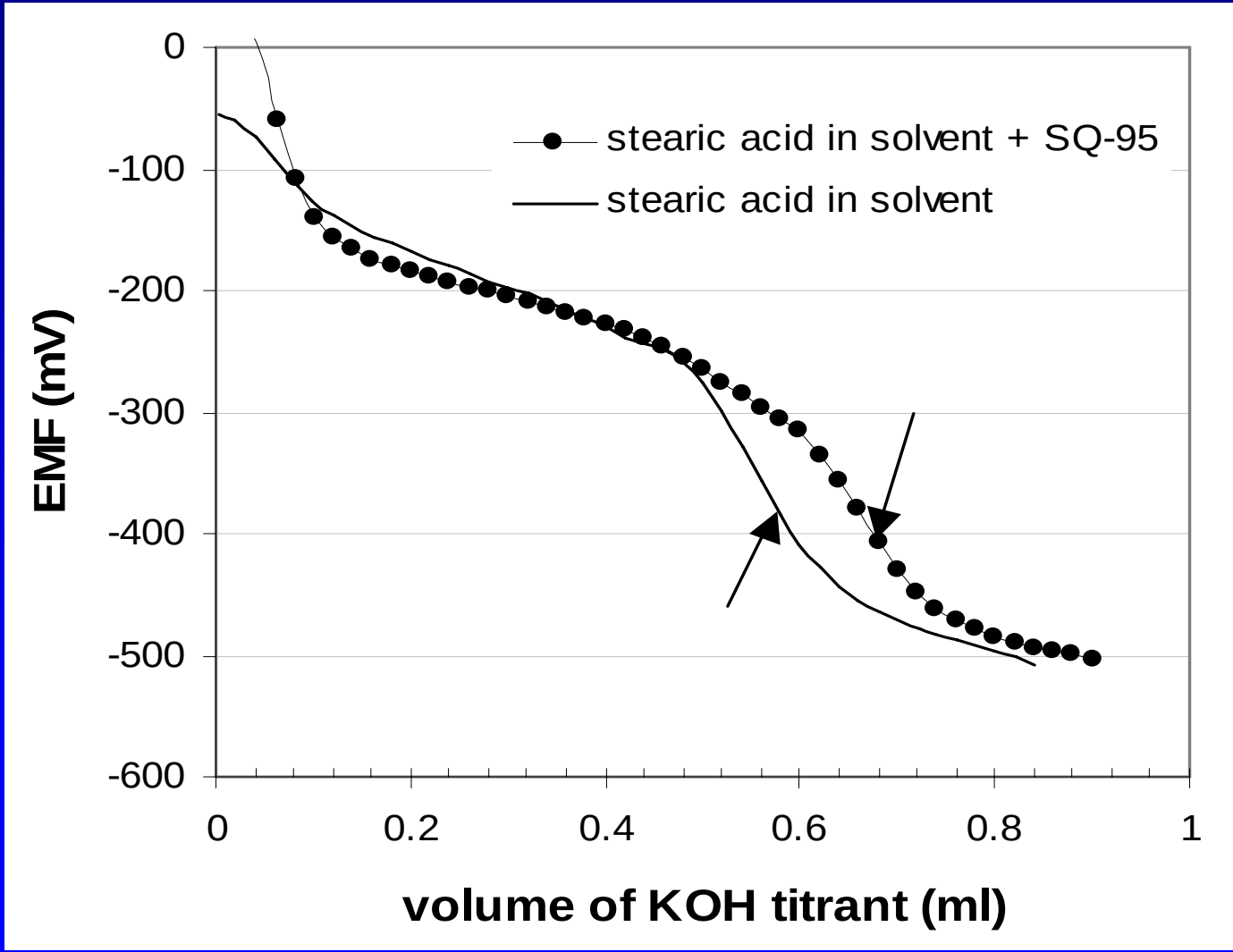
AN measurement improvements

- Spike the oil with stearic acid to enhance the titration inflection point.
- TBAOH as titrant (instead of KOH) confers stability on titration results.
- Recalibrate electrode(s) to compensate for changes after contact with crude oils.
- Revised procedure requires less oil (~0.5-1g).

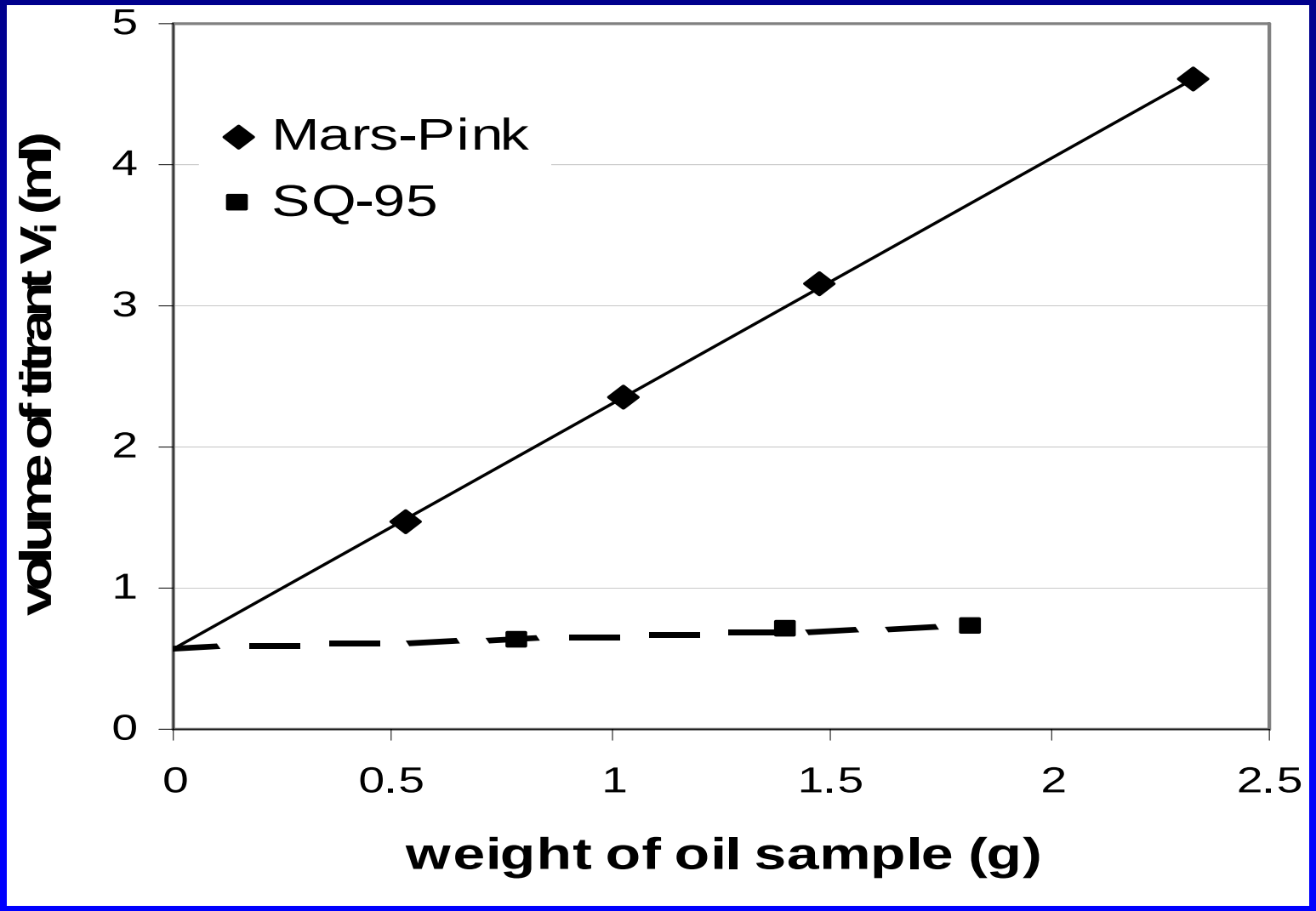
Oil Properties

Oil	API Gravity	Viscosity (cP)	Resins (wt%)	Asph (wt%,C_6)	BN	AN
Mars-P	16.6	481	25.8	6.0	2.30	3.92
MY-4	28.1	21.6	9.9	1.1	1.23	0.22
SQ-95	37.2	5.84	13.9	2.6	0.62	0.17

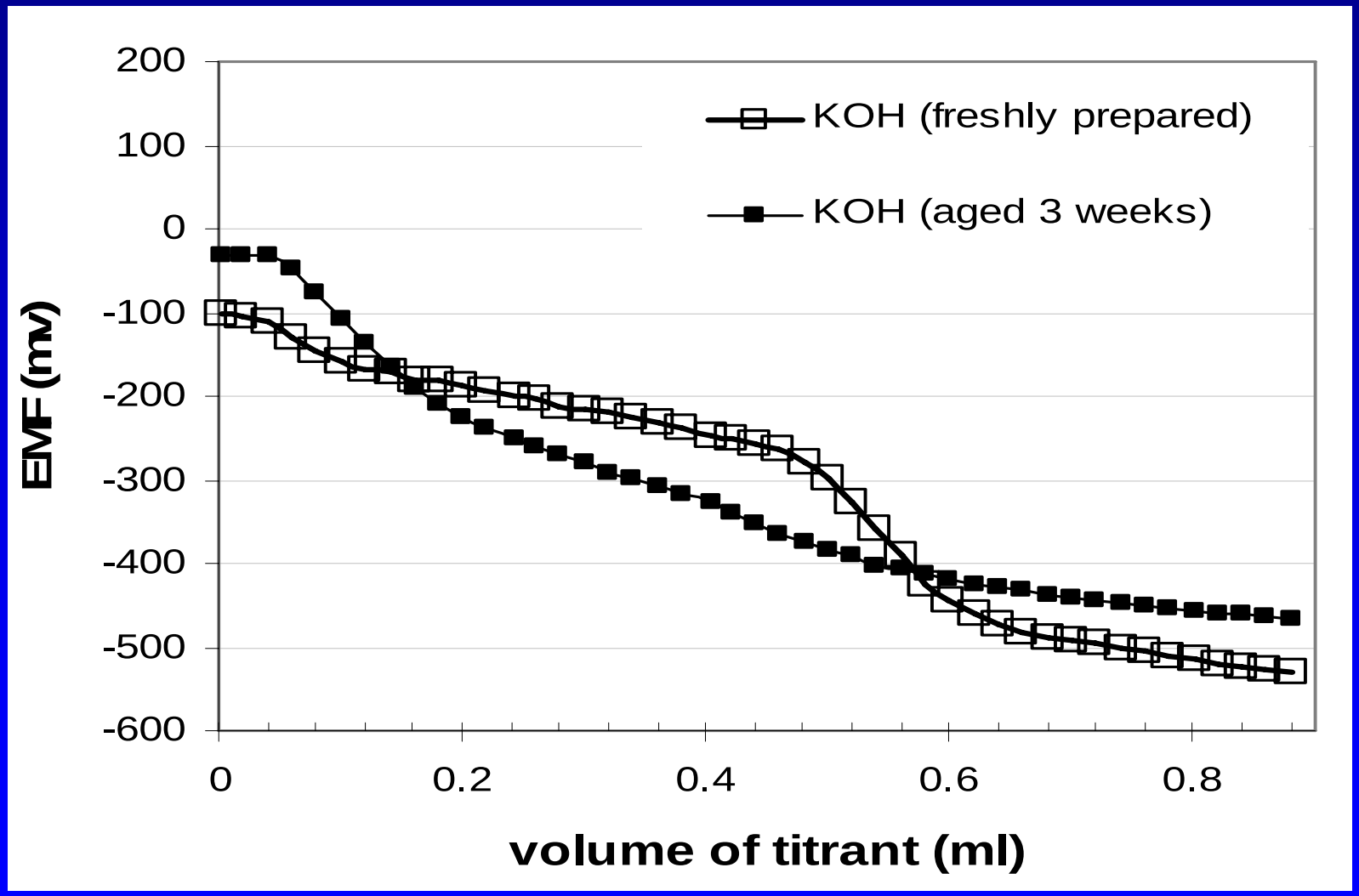
SQ-95 Oil Spiked with Stearic Acid



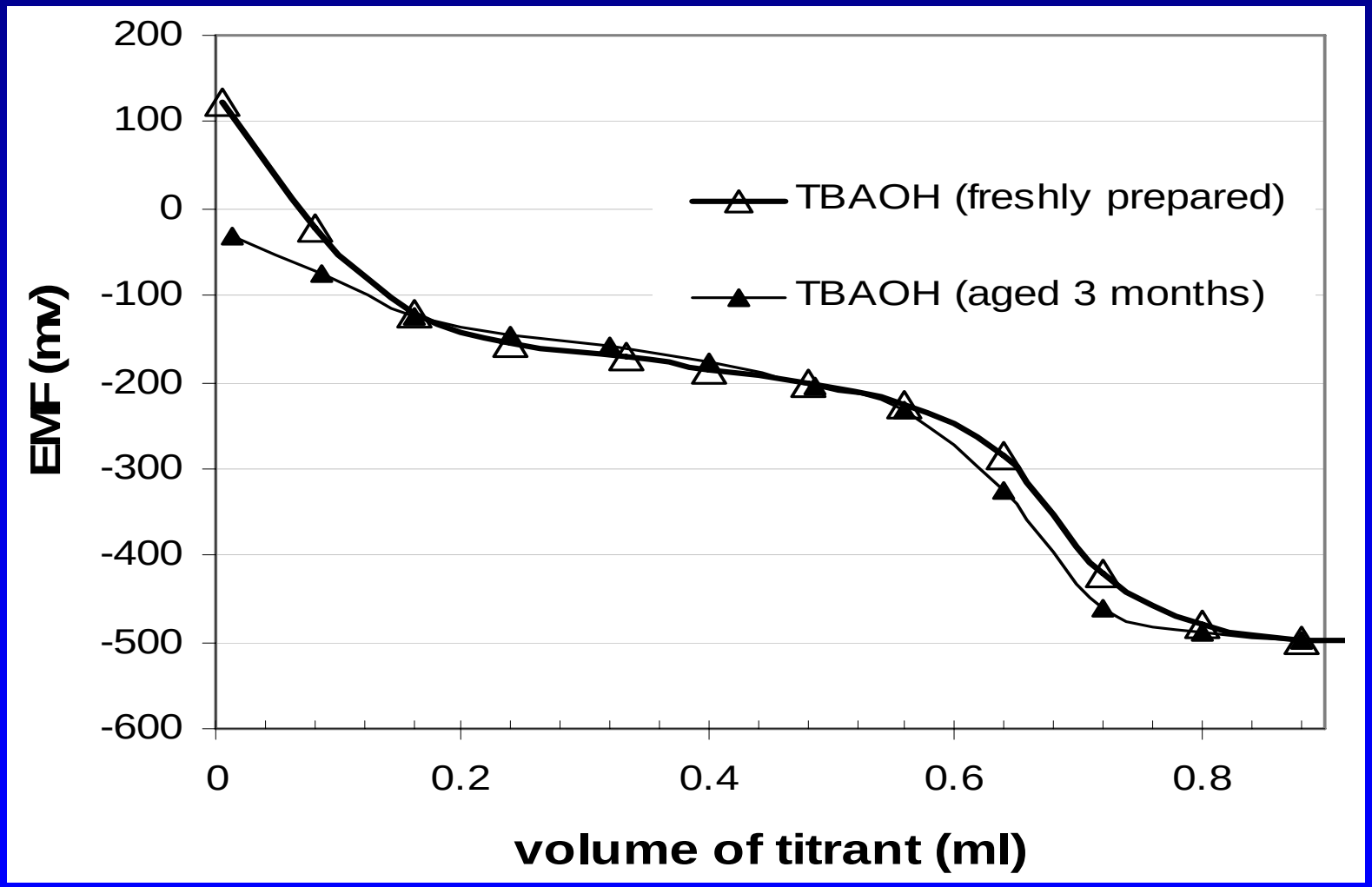
Oil Amounts versus Spike



Comparison of Fresh and Aged KOH as Titrant



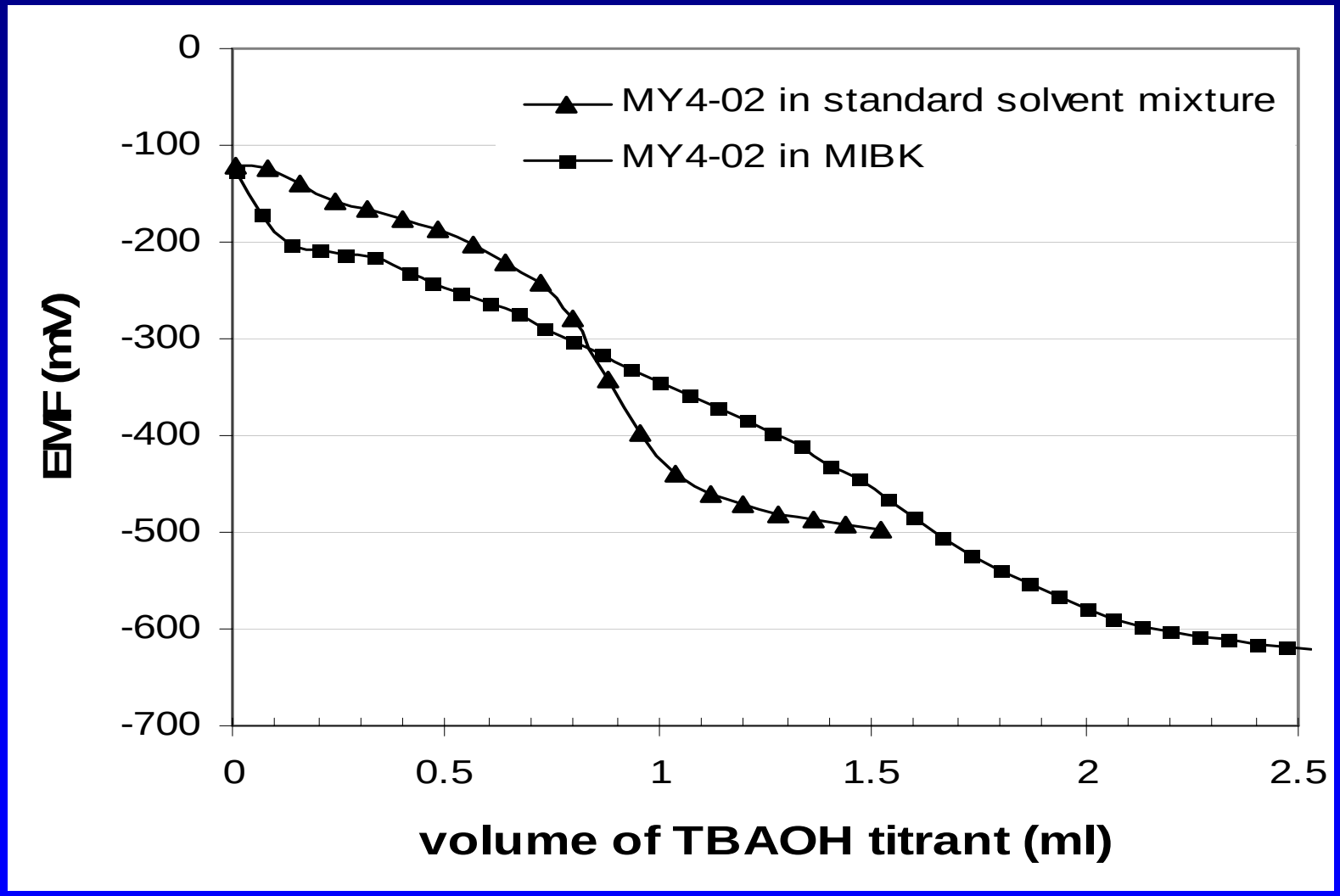
Comparison of Fresh and Aged TBAOH as Titrant



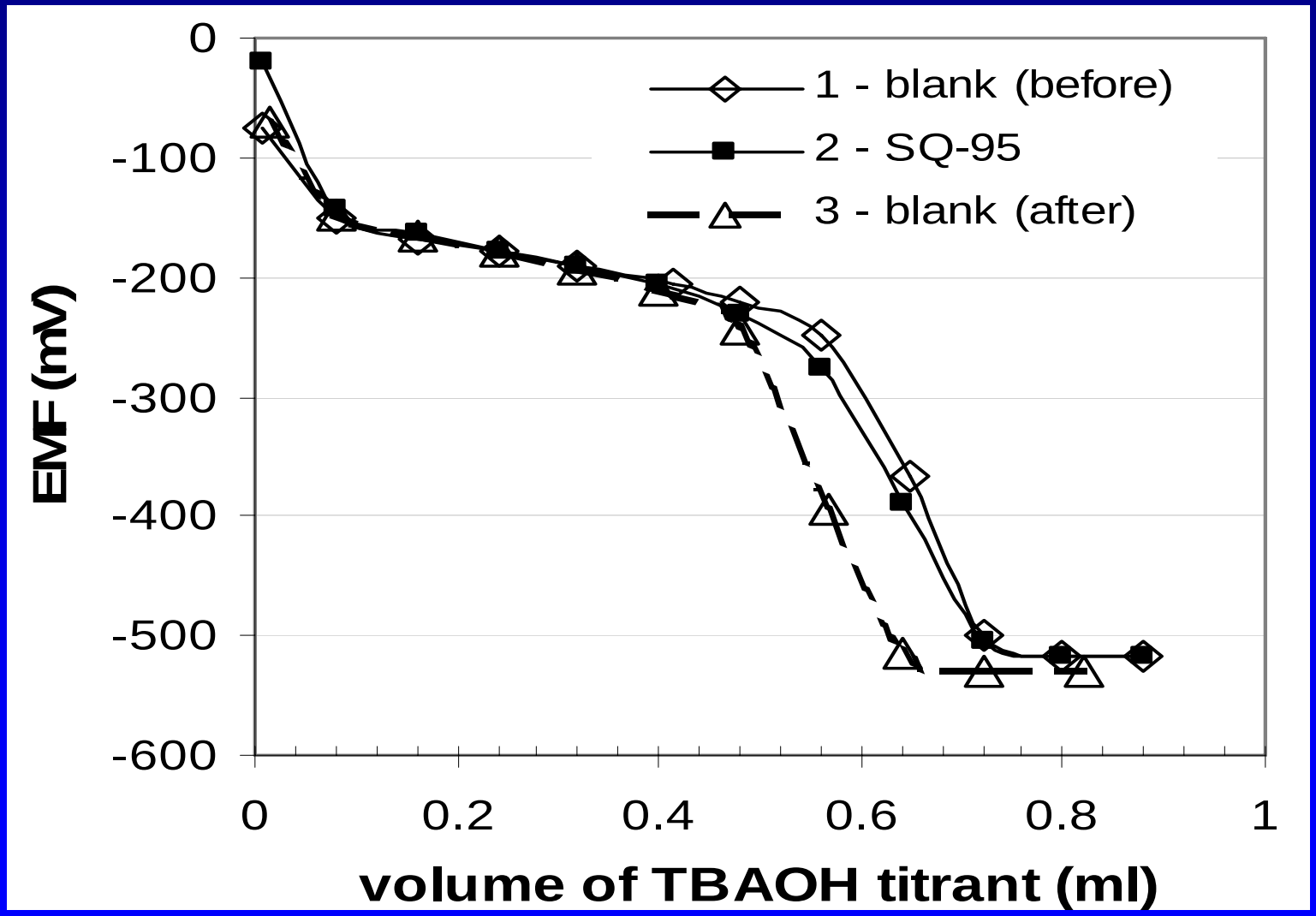
AN Measured with Different Titrant

Oil	Titrant=KOH AN (mg KOH/g oil)	Titrant=TBAOH AN (mg KOH/g oil)
Mars-Pink	3.92 STD=0.05	3.95 STD=0.02
SQ-95	0.17 STD=0.02	0.22 STD=0.02

Impact of Solvent on Titration



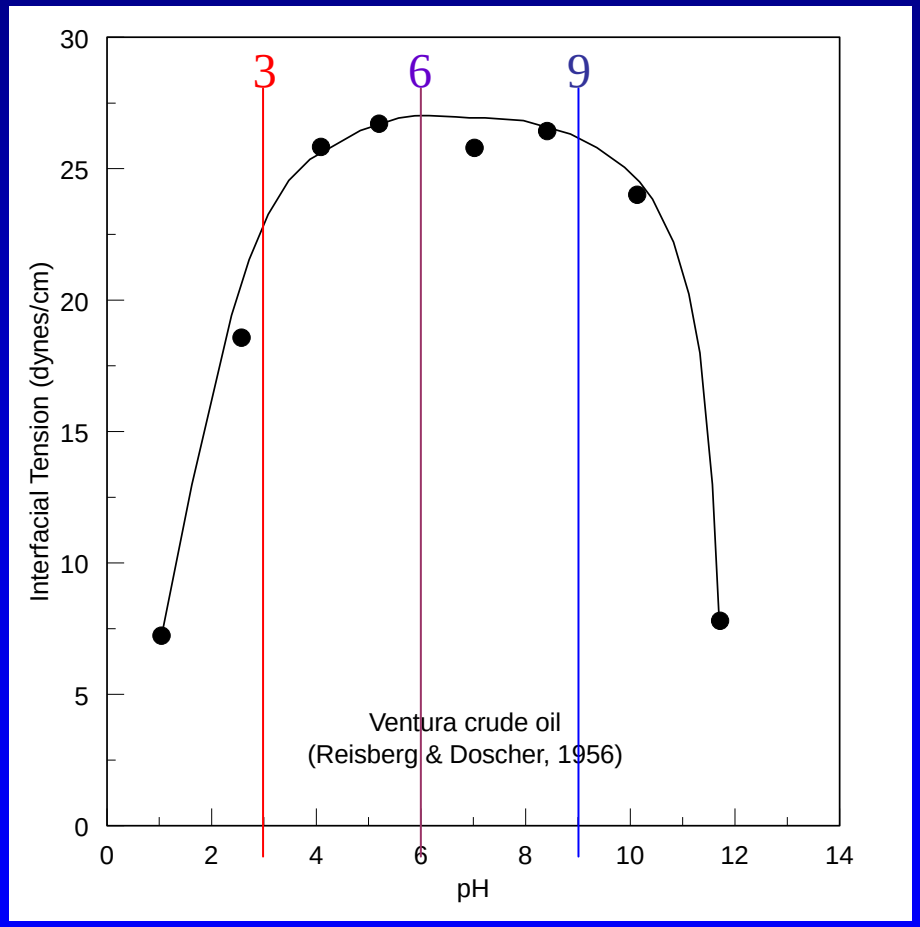
Electrode Response



Oil properties measured (CO-Wet database)

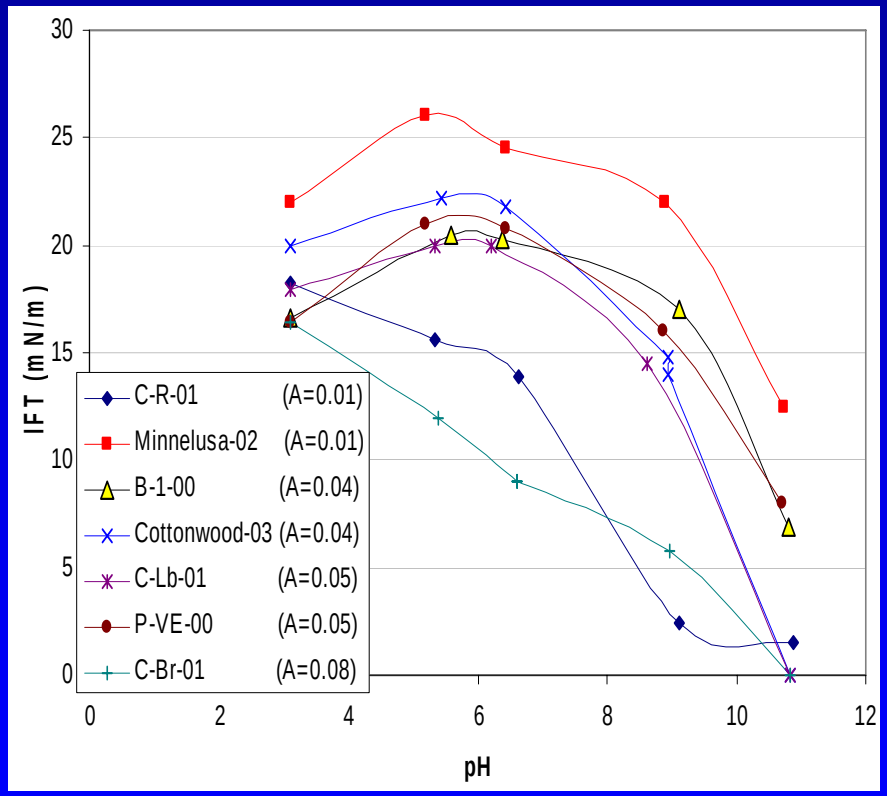
- density, ρ (and API gravity)
- viscosity, μ (and log μ)
- average MW
- RI
- P_{RI} (related to asphaltene stability)
- Saturates
- Aromatics
- Resins
- Asphaltenes (n-C_6 an n-C_7)
- Acid #
- Base #
- Isoelectric Point

IFTs measured as a function of pH

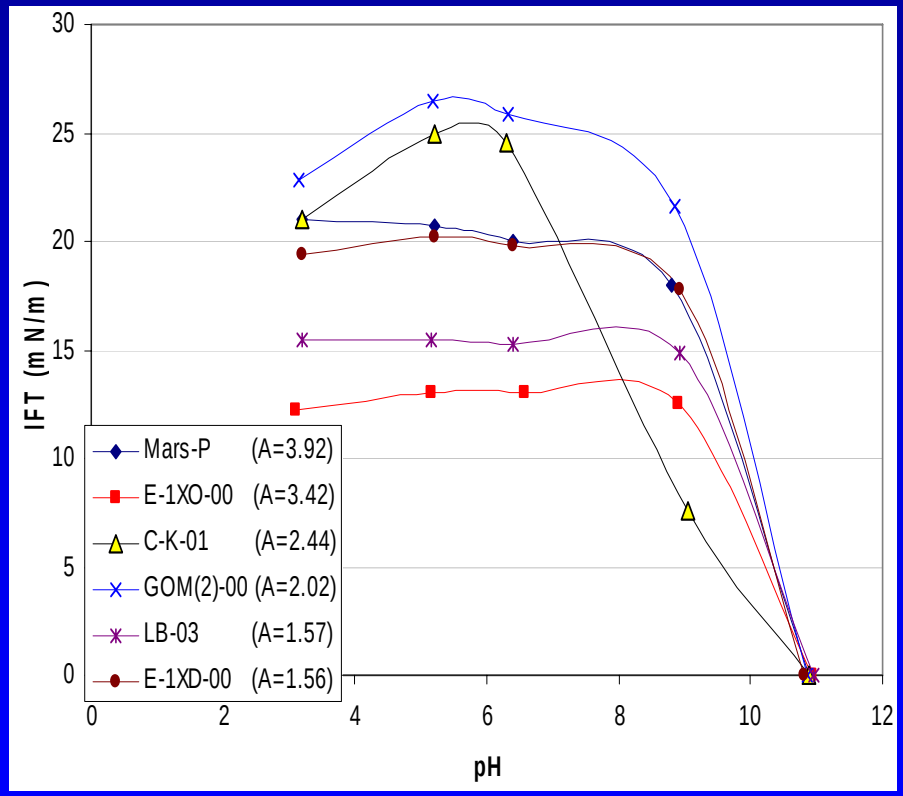


IFT vs. pH for Oils with Different AN
(SCA 2005-01)

AN < 0.1 mg KOH/g oil



AN > 1.5 mg KOH/g oil



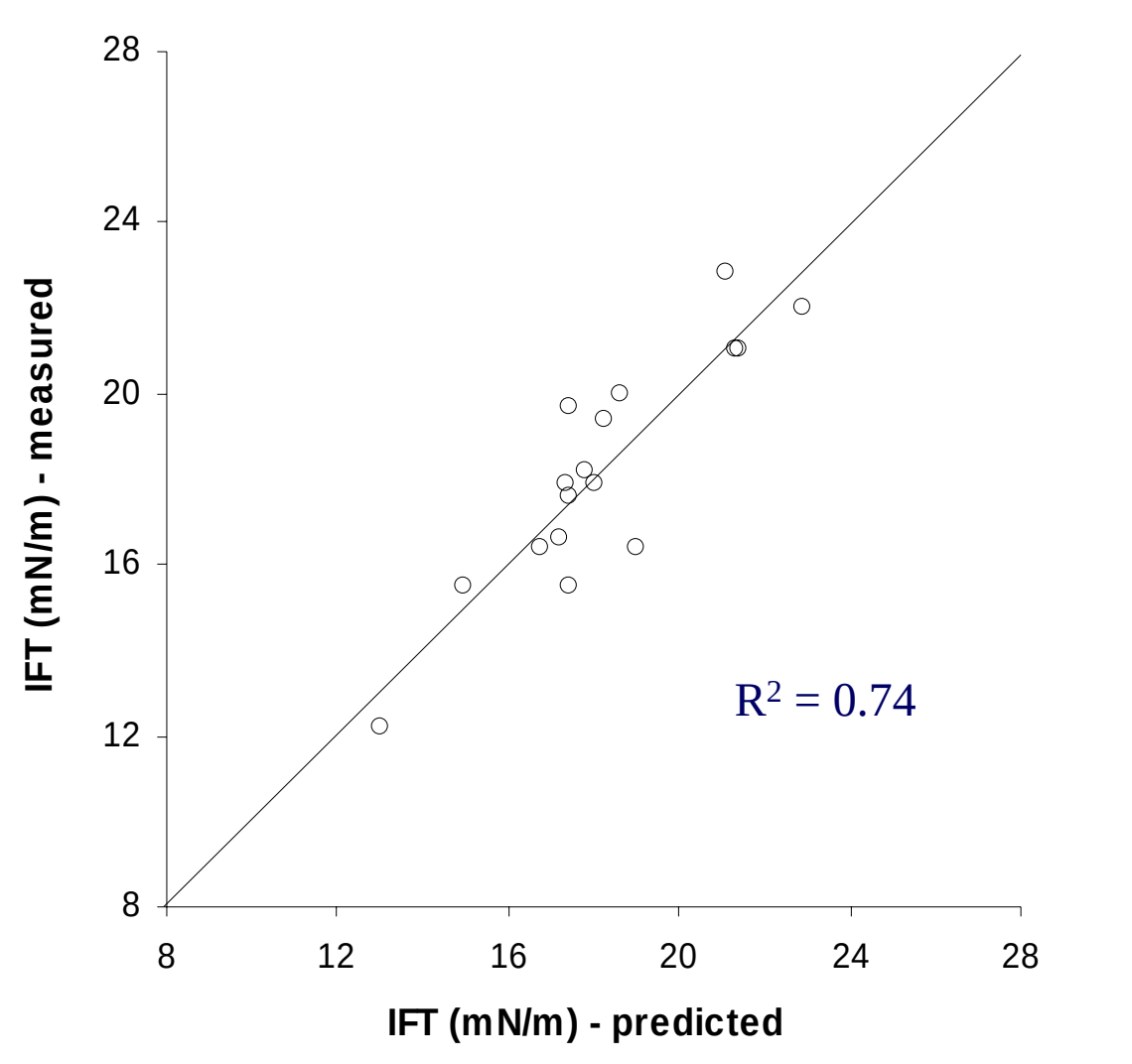
IFT correlations with crude oil properties*

pH	NaCl	Asph	A	B	μ
3		+	-		+
3	0.1	+	-		+
6		+	-	+	+
6	0.1	+		+	
9		+		+	
9	0.1	+		+	

*based on γ_{eq}

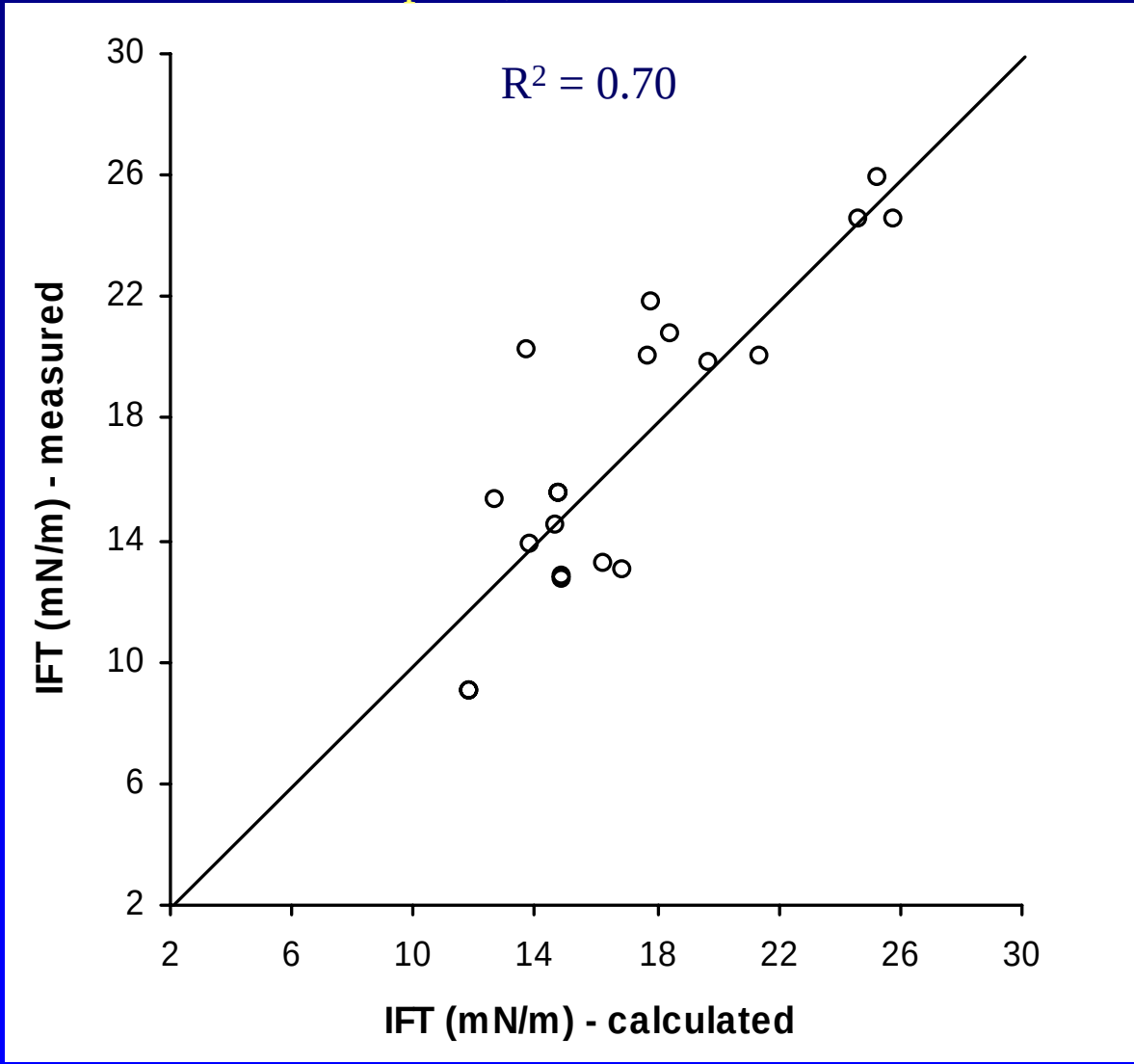
IFT correlation

pH 3, 0.1M NaCl



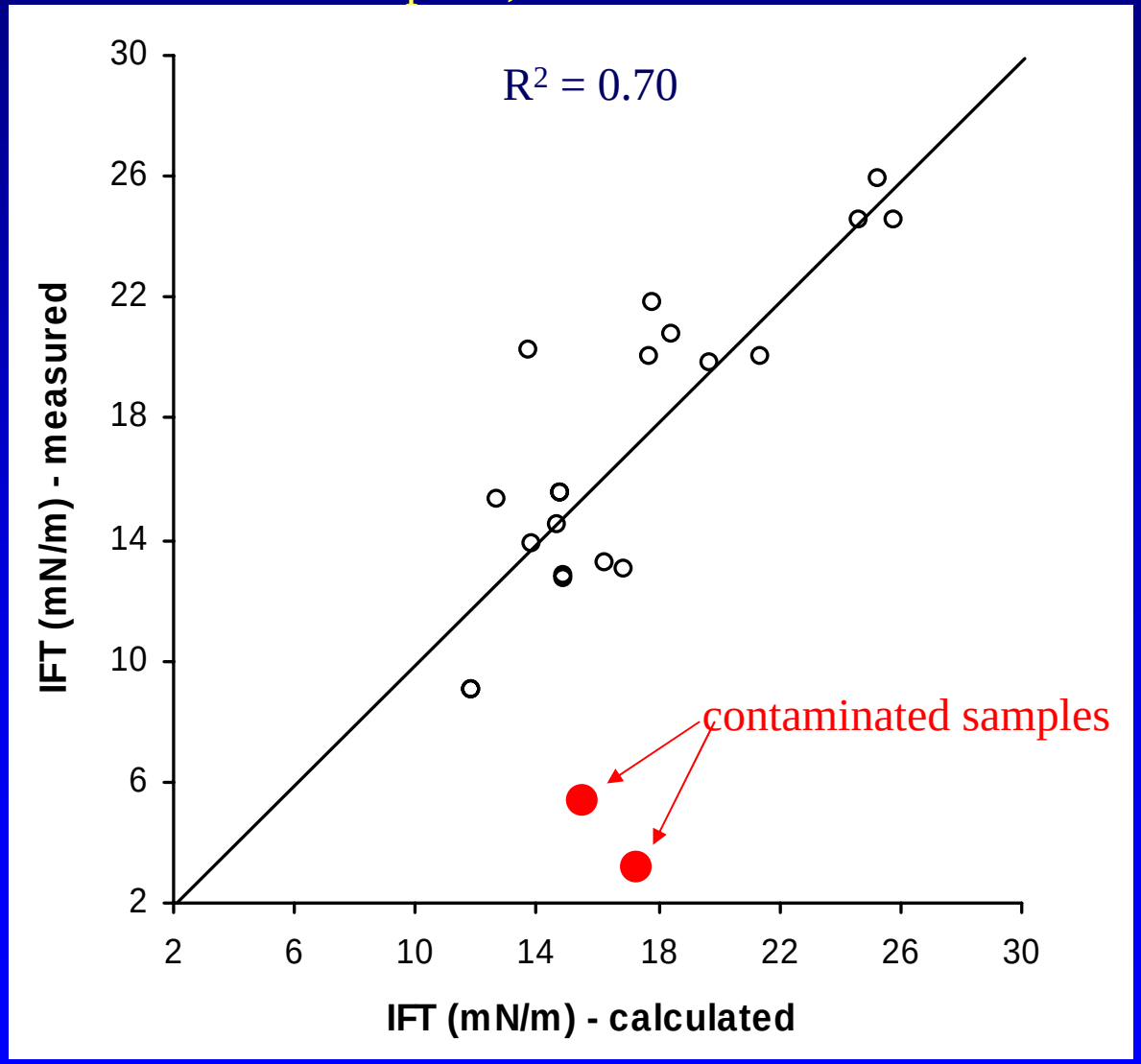
IFT correlation

pH 6, 0.1M NaCl



IFT correlation

pH 6, 0.1M NaCl



Summary

- AN measurement improved by spiking with oil-soluble acid.
- Forcing end point means less sample is required.
- Titrant stability improved by replacing KOH with TBA OH.
- No improved solvent was found. MIBK is not a good solvent for AN measurements.
- Blank measurements are affected by contact of electrode with crude oil.
- Carefully measured AN values correlate with crude oil interfacial properties.

Acknowledgements

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Stéphanie Monsterleet who first explored adaptations of the ASTM procedure by spiking crude oils with stearic acid

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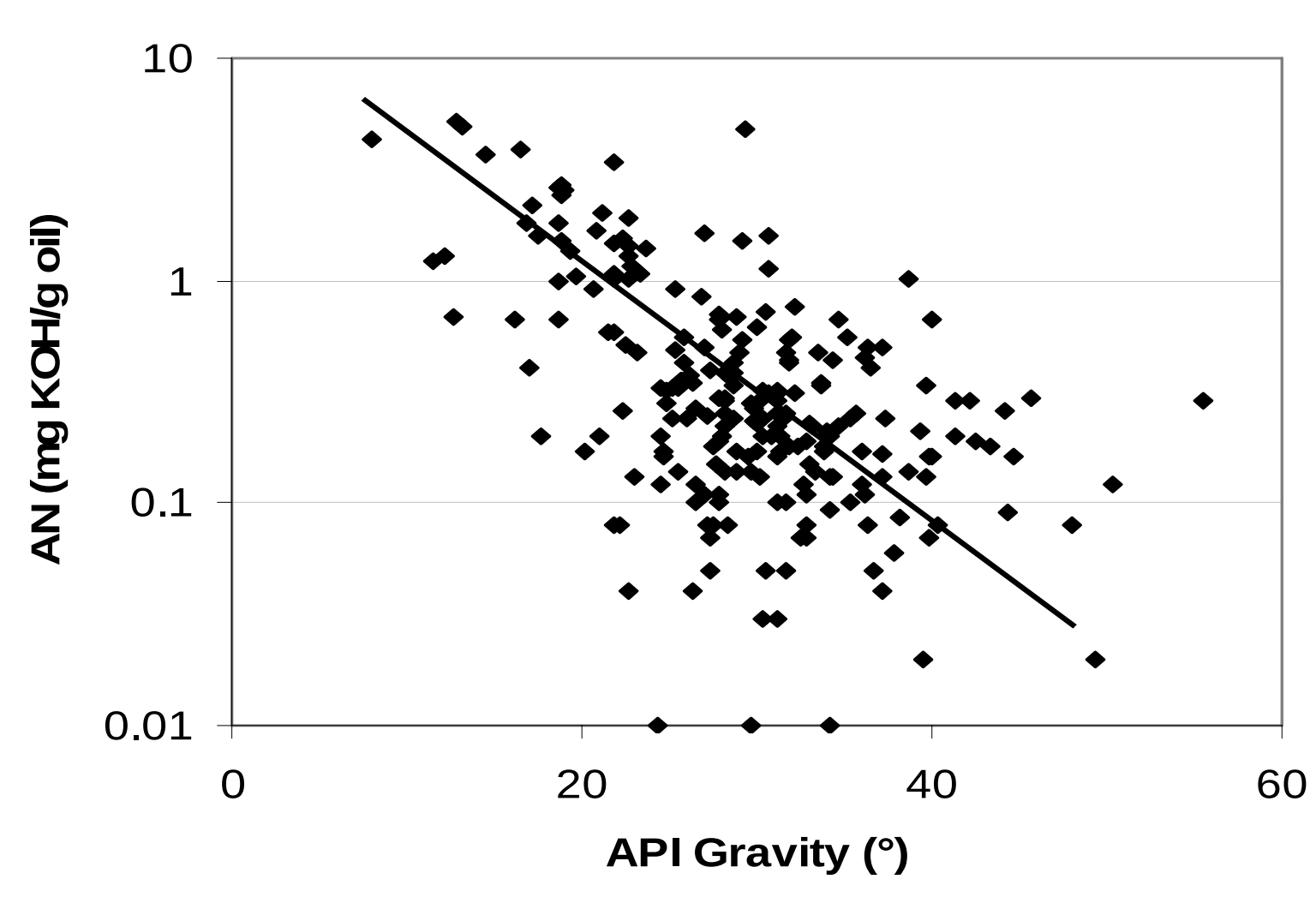
AN as a function of API Gravity