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Corrosivity of High Acid Crudes

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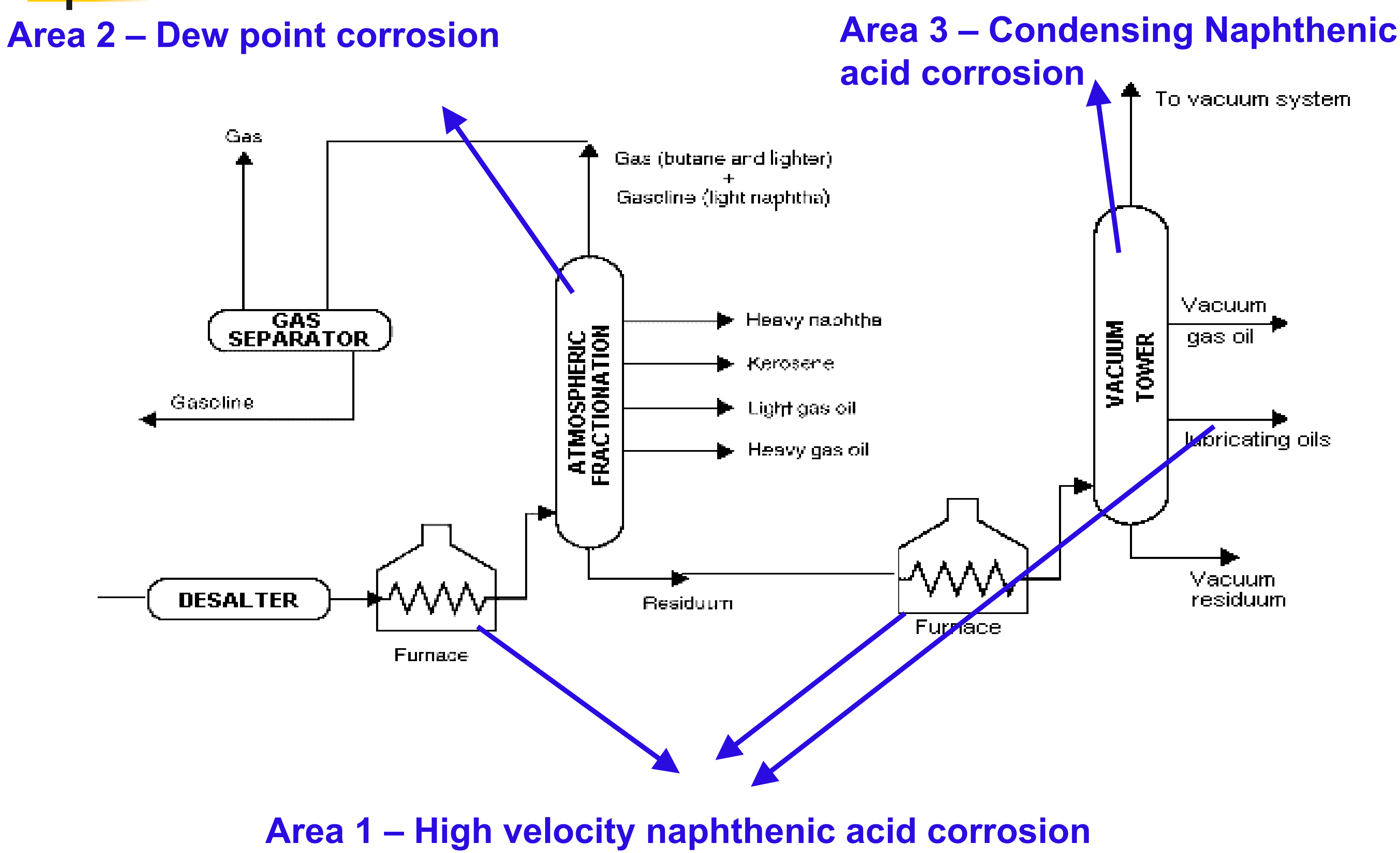
Introduction

- Crude purchase is the main expense of a refinery. Thus, processing discounted HAC have a positive financial impact.
- World production of high Acid Crudes (HAC) is expected to increase to 10-15% by 2010 and processing HAC will soon be a necessity rather than a choice.
- HAC may accelerate corrosion, fouling, furnace coking, desalting problems and need to be understood before processing them.
- Focus of presentation is about available tools for predicting corrosion impact of HAC in the distillation unit.

Corrosion in Distillation Unit (1)



Corrosion in Distillation Unit (2)

Area 1 - Furnace, transfer lines and side cuts

- Classical naphthenic acid corrosion affected by:
  - Temperature
  - Material of construction
  - Acid content
  - H_2S content
  - Shear stress (velocity)
- At high shear stress, a small amount of acid can increase rapidly H_2S corrosion (e.g. high corrosion even at TAN lower than 0.5)
- At low shear stress, H_2S may inhibit acid corrosion.

Corrosion in Distillation Unit (3)

Area 2 – Overhead or Dew Point Corrosion

- Hydrochloric acid, formed from the hydrolysis of calcium and magnesium chlorides in the crude, is the principal strong acid responsible for corrosion in crude unit overhead. Software is available to calculate water dew point at several levels of HCl. Neutralizer and corrosion inhibitors are injected.
- Carbon dioxide and low molecular weight acids are released from HAC. They buffer the acid solution formed and require more neutralizer inducing fouling.
- Released hydrogen sulfide, increase significantly dew point requiring a change in injection point.

Corrosion in Distillation Unit (4)

Area 2 – Vacuum Unit Corrosion

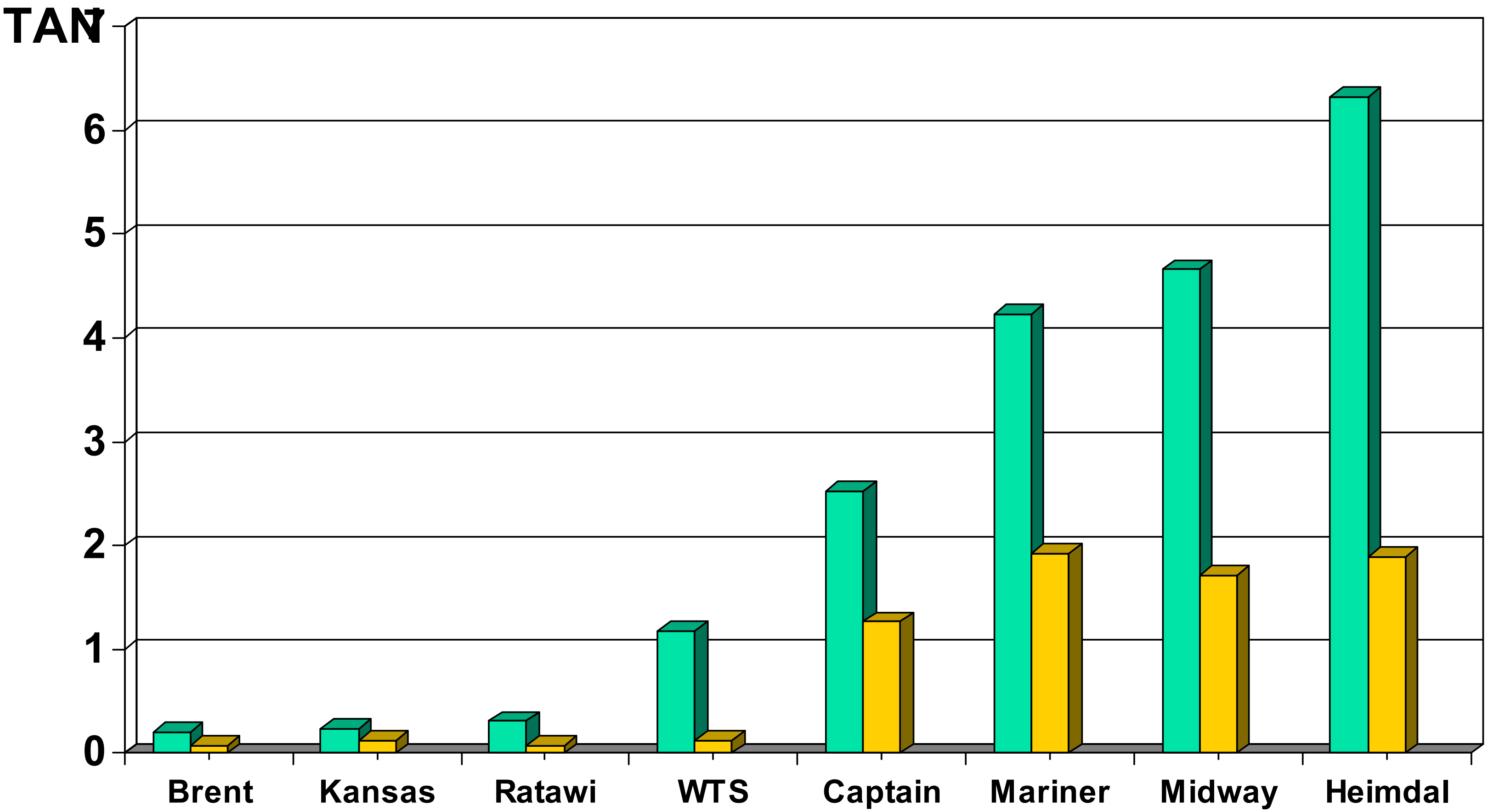
- Condensing naphthenic acid corrosion affected by:
  - Temperature
  - Material of construction
  - Acid content
  - H_2S content
- A high H_2S content is needed to inhibit naphthenic acid corrosion. Thus, need to blend HAC with crude having high H_2S release at 700+.
- No or little effect of shear stress .

Acids Analysis

- **Total acid number per ASTM D664**

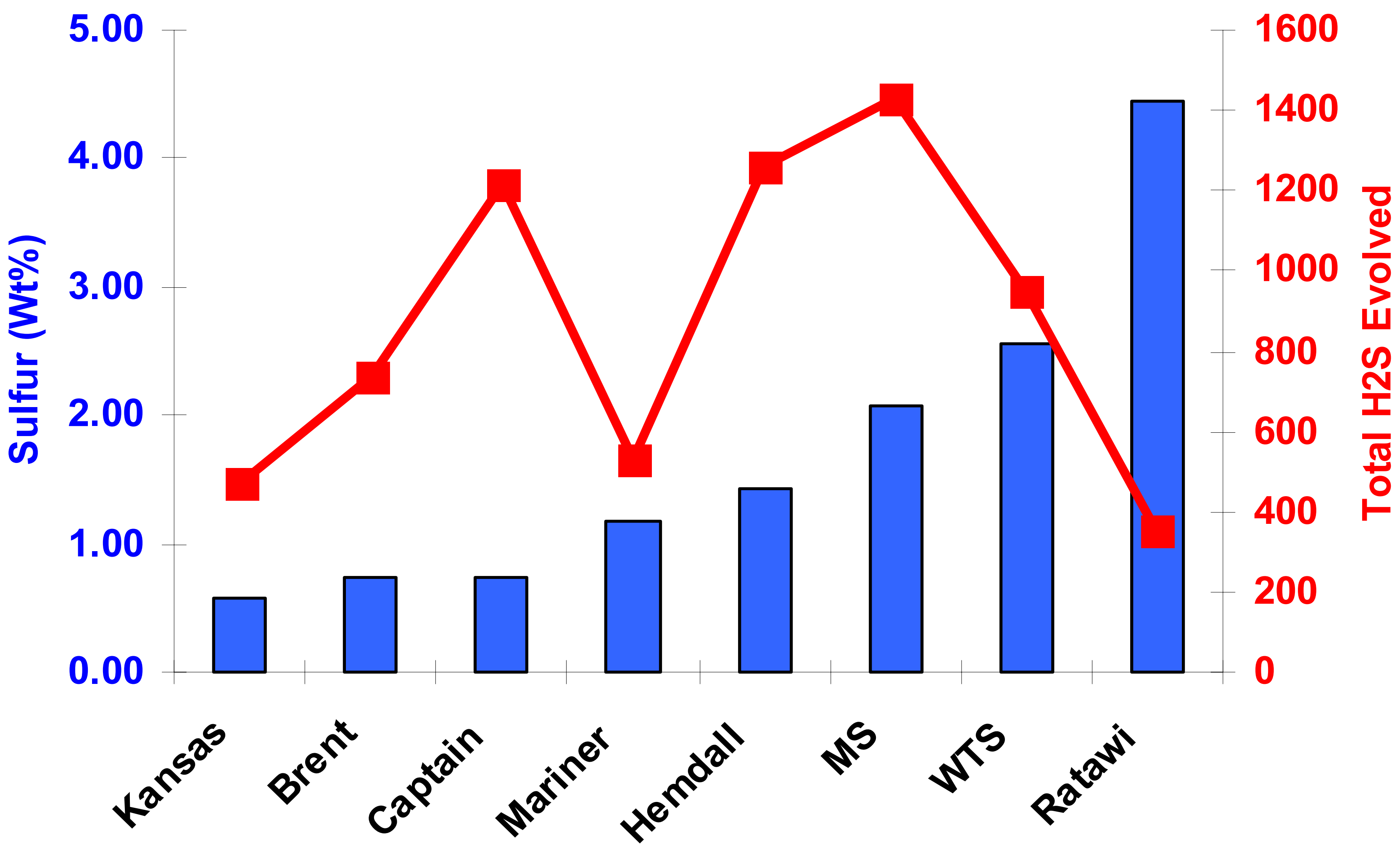
  Current method using potentiometric titration of a small amount of oil with alcoholic KOH.
- **Mobil Method # 1463-89 - Extraction of the acids by chromatography then analysis by FT-IR.**
- **Electrospray Ionization-Mass Spectrometry - Extraction of the acids by chromatography then analysis by EI-MS.**

Total Acid Number

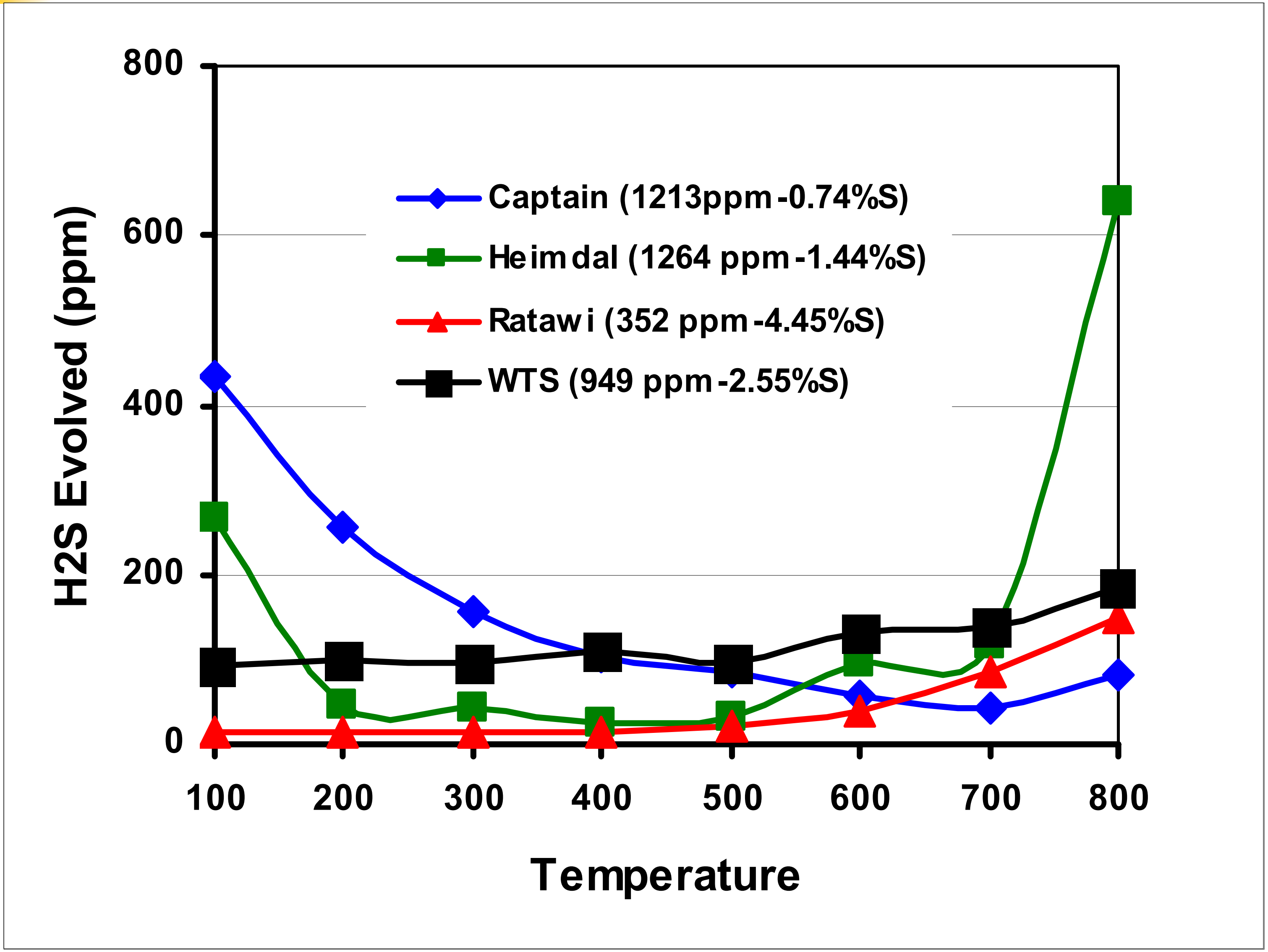


Sulfur %	0.74	0.58	4.45	2.55	0.74	1.17	2.08	1.44

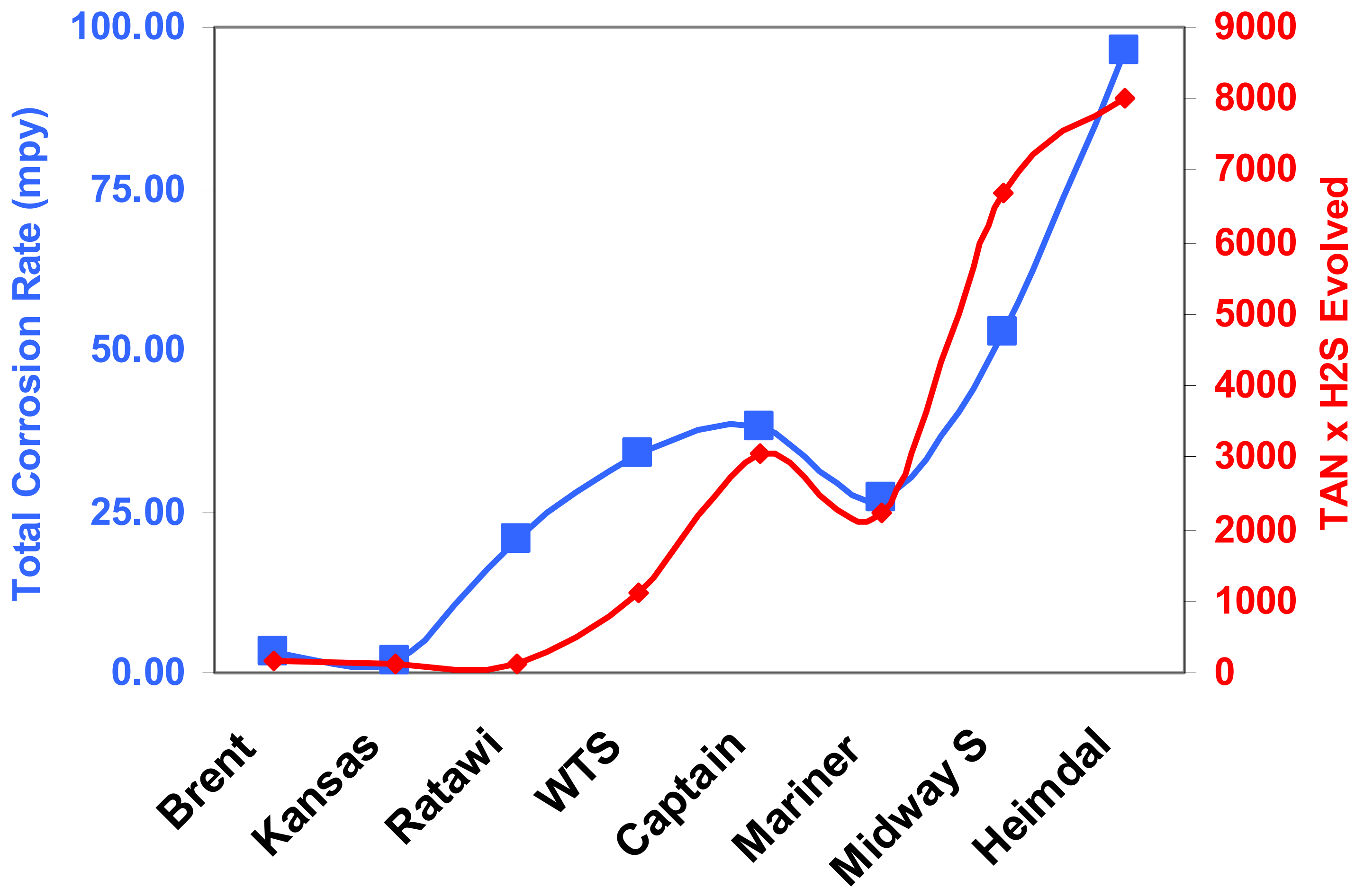
Sulfur Content vs. H_2S Evolution



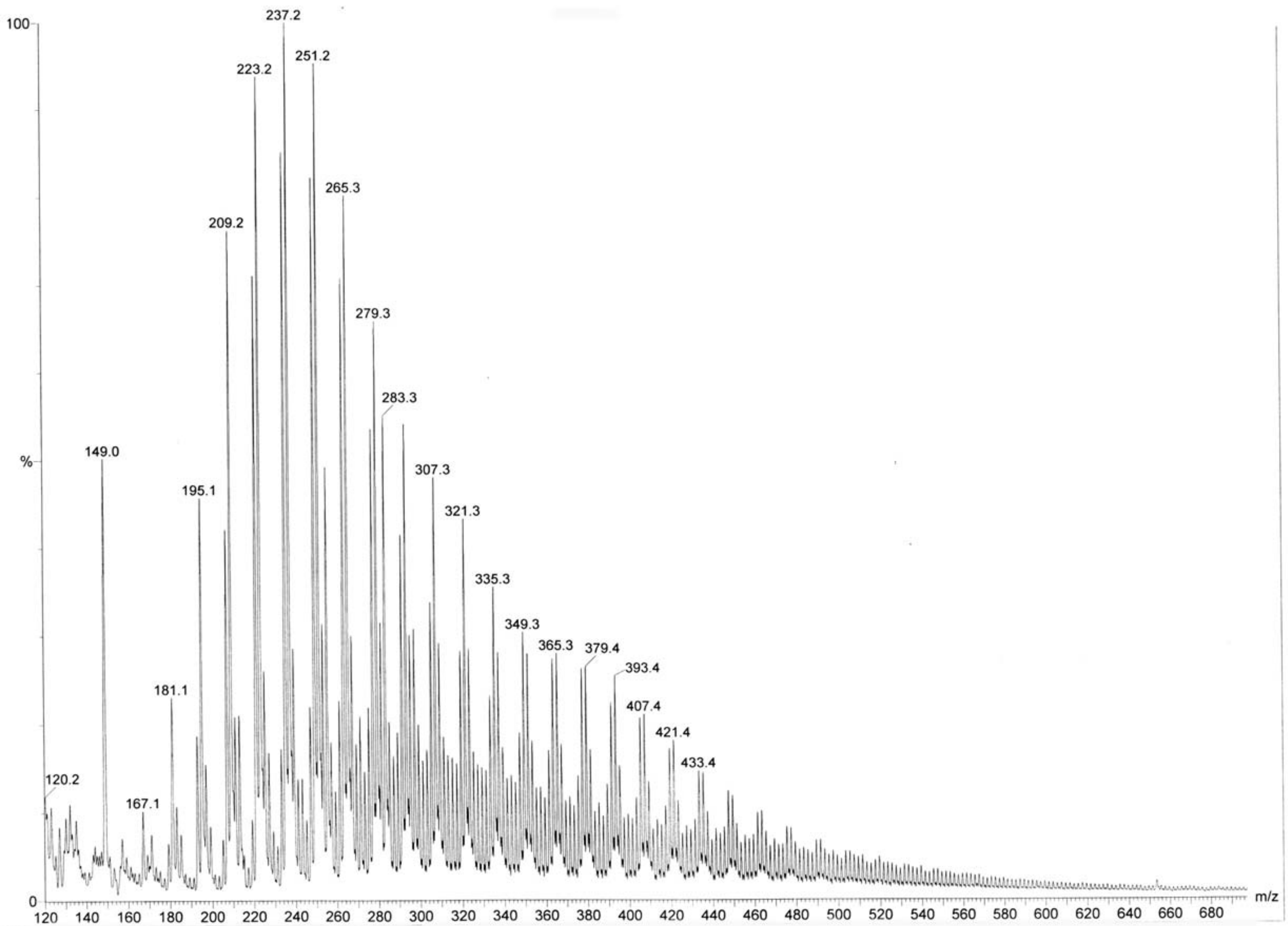
H_2S Evolution Analysis



Corrosion Test Results (1)



EI-MS of Captain Crude



Captain Crude

	Whole Crude	Light Naphta	Medium Naphta	Heavy Naphta	Kero	Atm Gas Oil	Light VGO	Heavy VGO	Vacuum Resid	Atm Resid
Temp at Start (F)	Start	305	305	305	400	500	650	850	1050	650
Temp at end (F)	End	305	305	400	500	650	850	1050	End	End
Sulfur (%)	0.70			0.04	0.10	0.27	0.56	0.75	1.15	0.83
Mercaptan (ppm)				11	7	5	4	3		
H2S (ppm)	834	156	156	101	84	57	123			
TAN	2.4			0.1	0.4	1.3	2.4	2.9		
Acid (% of total)				0.0	6.0	29.2	44.9	15.8	4.41	65

Ratawi Crude

	Whole Crude	Light Naphta	Medium Naphta	Heavy Naphta	Kero	Atm Gas Oil	Light VGO	Heavy VGO	Vacuum Resid	Atm Resid
Temp at Start (F)	Start	305	305	305	400	500	650	850	1050	650
Temp at end (F)	End	305	305	400	500	650	850	1050	End	End
Sulfur (%)	3.88	0.01	0.08	0.33	0.98	2.42	3.50	4.20	6.96	5.41
Mercaptan (ppm)		274	597	258	72	29	8	0		
H_2S (ppm)	40	12	12	14	22	62	236			
TAN	0.14	0.0	0.0	0.0	0.0	0.0	0.0	0.1		
Acid (% of total)					15.8	48.0	26.7	6.1	3.7	36.4

Field Application

- The amount of H_2S and acid in each area of unit are additive and can be calculated knowing the proportion of each crude in a basket.
- The analysis of the oil or blend can then be used:
  - To change proportion of each crude to minimize corrosion in critical areas.
  - To add specific crude to basket. E.g. one that releases high H_2S amount at 700 +F to inhibit corrosion of vacuum unit.
  - To change injection point of neutralizer/inhibitor in overhead to account for higher dew point.
  - To evaluate the effect of adding a specific HAC on corrosion of distillation unit.

Conclusions

- **There is <u>no</u> correlation between total sulfur content and H_2S evolved.**
- **H_2S evolution data analysis allows the determination of the specific concentration of H_2S in each area of the distillation unit.**
- **TAN values are higher than actual acid concentration especially if crude has a high sulfur content.**
- **Electrospray data analysis allows the determination of where the acids concentrate in the unit.**
- **H_2S and EI-MS analysis are simple, rapid and cost effective. Only a 100 ml of sample is needed. They yield critical information about corrosivity missing in a typical crude assay.**

Thank you for your attention

Any Questions ?