



Application Note AN-PAN-1026

Analysis of hydrogen sulfide and mercaptans derived from crude oil

Online determination according to ASTM D3227 and UOP163

Sulfur compounds in petroleum products not only have an unpleasant odor, but they are also environmentally damaging and promote corrosion. Desulfurization can occur at many points within a refinery – from the crude feedstock to the distillate streams. While lighter impurities (including mercaptans and sulfides) can be removed via hydrotreating, heavier sulfur compounds can be removed with hydrocracking after the hydrotreating process. This Process Application Note details the online

analysis of hydrogen sulfide and mercaptans by potentiometric titration. Many areas within the refinery can benefit from the implementation of a Metrohm Process Analytics **2045TI Ex proof Process Analyzer** with a customized sample preconditioning system to ensure the catalysts in the reactors are not exhausted and to limit corrosion in the distillation unit. The analyzer fulfills EU Directives 94/9/EC (ATEX95) and is certified for Zone 1 and Zone 2 areas.

INTRODUCTION

Fossil fuels are known for their sulfur content, which originates from the decomposition of dead organisms over millennia. Mercaptans (thiols) and hydrogen sulfide (H_2S) are two sulfur compounds present in crude oil which contribute to its characteristic odor. In the refining process, these can lead to increased corrosion in distillation equipment at the high temperatures used. Additionally, excess sulfur dioxide ($SO_{2(g)}$, a pollutant) can be emitted after combustion if sulfur is present in the refined products. Therefore, it is best to remove as much sulfur as possible early on in the refining process. Sulfur compounds are present throughout the

entire boiling range of hydrocarbons in crude oil. Depending on the size and bond strength of these compounds, different desulfurization treatments are available. Lighter impurities (including mercaptans and sulfides) can be removed *via hydrotreating* in a reactor with a catalyst (generally cobalt molybdenum) and hydrogen under high temperature and pressure. Heavier sulfur compounds can be removed with *hydrocracking* after the hydrotreating process. **Desulfurization (Figure 1)** can occur at many points within a refinery, from the crude feedstock to the distillate streams.

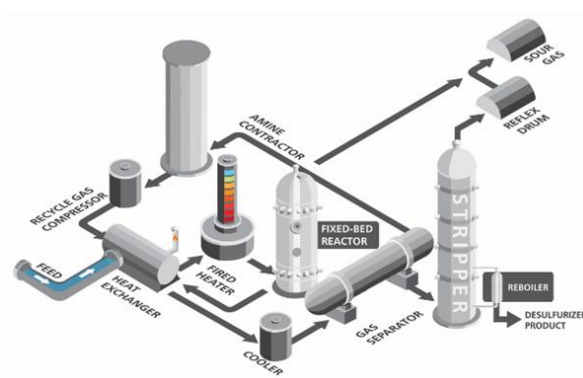


Figure 1. Schematic diagram of a typical hydrodesulfurization (HDS) unit in a petroleum refinery.

Traditionally, the oil and oil product analysis can be monitored by laboratory titration with silver nitrate using a sulfide-coated silver electrode serving as the indicator electrode. However, this methodology does not provide timely results and requires human intervention to implement the results of the laboratory analysis into the process. Online process analysis allows constant monitoring of oil quality without long waiting times in the laboratory, providing more accurate and representative results directly to the control room for quick process adjustments.

By using online process analyzers, operators gain the most representative, up-to-date information they need to accurately identify trends, reduce

downtimes, and address operational issues before costly problems arise. In addition, the time of response to corrosion formation is fast and immediate warnings are delivered in case of out-of-specification readings.

The Metrohm Process Analytics **2045TI Ex proof Process Analyzer (Figure 2)** with a customized sample preconditioning system could be implemented in many areas within a refinery to ensure that catalysts in the reactors are not exhausted and to limit corrosion further on in the distillation unit. The analyzer fulfills EU Directives 94/9/EC (ATEX95) and is certified for Zone 1 and Zone 2 areas.



Figure 2. The 2045TI Ex proof Process Analyzer is certified for Zone 1 and Zone 2 areas.

APPLICATION

The mercaptan and H₂S content in crude oil is determined by a two-endpoint argentometric titration based on ASTM D3227 and UOP163.

Endpoint 1 corresponds to H₂S and endpoint 2 to the mercaptans.

REMARKS

Other online applications are available for the petrochemical industry such as: salt in crude oil, ammonia, phenol, bromide index, saponification

value, halogens, acidity, and many more in different areas of a refinery (e.g., water in crude desalting).

Table 1. Oil refinery measurement parameters

Parameters	Untreated crude oil	Treated crude oil
Mercaptans	100–500 mg/L	0–50 mg/L
H ₂ S	0–100 mg/L	0–1 mg/L

CONCLUSION

Crude oil contains several percent by weight of sulfur compounds. They not only have an unpleasant smell, but they are also environmentally harmful and corrosive which is why they must be largely removed during refining. The 2045TI Ex proof Analyzer with a flexible sample pretreatment system is the ideal

solution for a very wide selection of petrochemical refinery applications. This process analyzer fulfills EU Directive 94/9/EC (ATEX95) and is certified for Zones 1 and 2. The 2045TI Ex proof Analyzer monitors mercaptan and H₂S content in crude oil in accordance with ASTM D3227 and UOP163.

RELATED APPLICATION NOTES

[AN-PAN-1001 Online analysis of hydrogen sulfide and ammonia in sour water stripper](#)

[AN-PAN-1014 Online determination of salt in crude oil by automated process analysis](#)

[AN-PAN-1037 Online thermometric titration of acid number \(AN\) in oils \(ASTM D8045\)](#)

[AN-PAN-1047 Inline monitoring of water content in naphtha fractions by NIRS](#)

[AN-PAN-1052 Online process monitoring of octane number during catalytic reforming by NIRS following ASTM D2699 and ASTM D2700](#)

BENEFITS FOR TITRATION IN PROCESS

- **Protection of company assets** with built-in alarms at specified warning limits to prevent corrosion
- **Safer working environment** for employees (e.g., no exposure of operator to dangerous and explosive environments)
- **Guarantee compliance** with environmental standards



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CONFIGURATION



ADI 2045TI Ex proof Analyzer

ADI 2045TI Ex 防爆型プロセスアナライザーは、防爆仕様が決定的重要性を持つ安全要求事項となるような危険な地域で使用されます。この装置はEU規定94/9/EG (ATEX95)を満たし、爆発の恐れのあるゾーンIおよびIIでの使用が認可されています。その構造は、空気清浄システムおよび過圧システムをそれに属する電子安全装置と組み合わせたものであります。空気清浄工程および持続的な過圧により、爆発性雰囲気内で空気が分析装置のハウジングに侵入するのを防ぎます。分析装置のインテリジェントな構造により、大型の分析装置保護設備の洗浄は不要で、また危険区域内にある製品ラインへの装置設置が可能となります。

滴定、カールフィッシャー滴定、測光法、イオン選択性電極による測定と並んで、このEx-pバージョンによる直接測定も可能です。