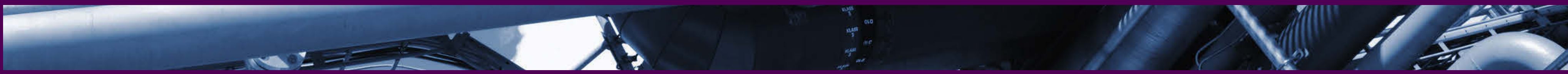
SULPHUR MONITORING IN OIL REFINERIES PRODUCTS



Sulphur is one of the most abundant non-metal elements used in a variety of industrial applications, including the production of sulphuric acid, explosives, rubber, fertilisers, pigments, dyes, insecticides, detergents, as well as many inorganic salts and esters production. Sulphur is equally present in petroleum at concentrations ranging between 0.05 to 14wt%. Given the fact that sulphur is naturally found in petroleum products, it is considered an undesired impurity since sulphur may form salts products during the crude processing, increasing the risk of product leakage during transportation and altering the catalyst activity during the refining operations. In order to control the sulphur concentration at different stages of hydrocarbon production, it is necessary to identify the critical point during the desulphurisation steps using appropriate analytical methods. Dry colorimetric method provides an option for sulphur monitoring at different concentration levels.

Introduction

Modern refineries integrate industrial treatment plants with adequate quality control practices to obtain a wide variety of products controlling the efficiency of the operations. These operations involve physical and chemical processes, to convert the crude oil into higher value products, including but not limited to distillation, extraction, reforming, hydrogenation, cracking and blending. Gasoline, liquid petroleum gas (LPG), jet and diesel fuels waxes, lubricants, bitumen and other petrochemical products are the main products derived from oil. Emerging technologies in this field seek to optimise and to increase the yield of the refining processes meeting the environmental restrictions in terms of the transportation of fuels and the emissions as products of the refineries operations itself[1].

Sulphur, oxygen, nitrogen and some metals compounds are grouped in the hetero atoms commonly found in petroleum products. Sulphur in crude oils is present in the form of organosulphur compounds as mercaptans, mono-and disulphides with alkyl radical chains and thiophenes. Mono- and disulphides are not corrosive in contrast to mercaptans. In spite of a wide variety of organic sulphur compounds, hydrogen sulphide (H_2S) is the predominant inorganic sulphur form given the low thermal stability of its organic forms during crude processing. H_2S is a corrosive gas at high humidity levels and high temperatures. In petroleum fuel products, sulphur oxides (SO_x) may be formed during combustion and they constitute a relevant environmental concern because they are considered air pollutants.

Elemental sulphur is recovered from natural gases with high H_2S content via the Claus process. The process consists of multistage catalytic oxidation of H_2S. Each catalytic stage consists of a gas re-heater, a catalyst chamber and a condenser [2]. The gas stream leaving the Claus unit enters a tail gas treating unit with a total elemental sulphur recovery near 99.8% in order to comply with the sulphur emissions environmental standards [3]. Worldwide regulatory organisms (Directive of the European Parliament, the Environment Protection Agency (EPA), Environment Canada) direct their policies to decrease the sulphur content to 30-50 ppm in gasoline and diesel since January 2005. In fact, the zero-emission or ultra-low sulphur levels in fuels are expected. Desulphurisation technologies and critical point monitoring is mandatory to achieve the ultra-low sulphur content [4]. In addition, sulphur in contact with metal pipeline surfaces (transporting the oil and gases at different locations inside the refineries) results in an H_2S corrosion reaction, which acts as a catalyst to promote adsorption of atomic hydrogen into the corroding steel [5].

Whether to comply with environmental standards or to control process efficiency under safety practices, it is mandatory to monitor the sulphur content at ppm and ppb levels. Dry colorimetric method offers a reliable and affordable solution with accurate and repeatable results in different matrices including liquids and gases. Detection is performed using chemically impregnated filter paper with humidified lead acetate that provides good sensitivity and specificity to H_2S gas. Total sulphur content in hydrocarbons based matrices consists in the conversion of organically bound sulfur compounds into H_2S by reduction with hydrogen. The method does not require sophisticated components or extensive maintenance protocols for good performance. The technique is adapted to comply with ASTM methods: D4045, D4468 and D4084.

Results

Dry colorimetric detection for total sulphur content is suited for different matrices including gases, LPGs and liquid hydrocarbons at different concentration ranges from low ppb to percentage content of sulphur. Figure N.1 presents results for different organic solvents representative of fuel matrices, gasoline, naphtha and diesel. According to these results the calibration curve presents good linearity correlation between zero and 1 ppm total sulphur.

Results for total sulphur testing in gases using dry colorimetric method present a linear detector

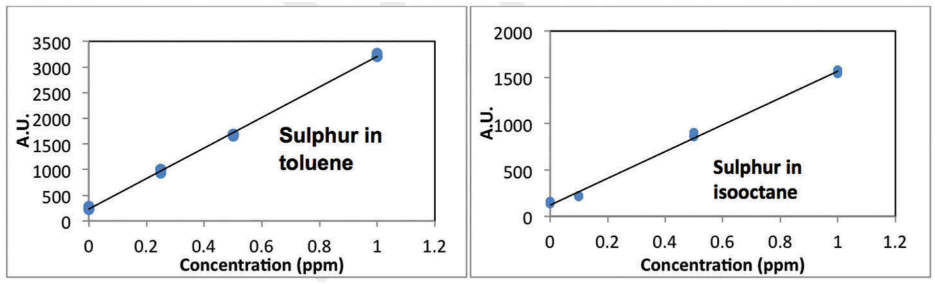


Figure 1: Total sulphur content in different organic solvents at concentration values below 1ppm.

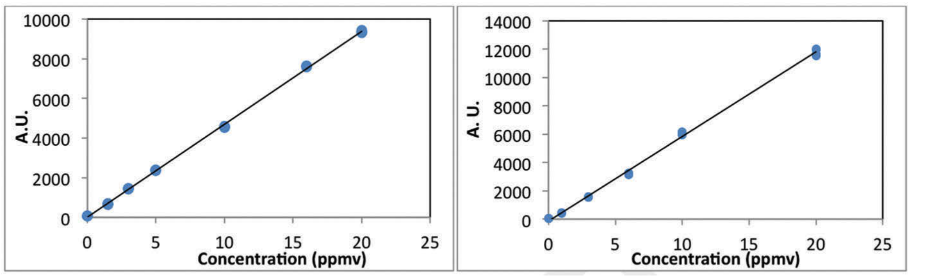


Figure 2: Hydrogen sulphide in nitrogen (left); total sulphur content using COS in nitrogen (right).

response at ppm levels as well. Figure N.2 exemplifies a typical linear trend for concentrations up to 20 ppm performing multiple loop injections of hydrogen sulphide and carbonyl sulphide in nitrogen. Carbonyl sulphide was measured reducing it to hydrogen sulphide via reaction with hydrogen at high temperature. For both cases, the time of response is less than 5 minutes for analysis. In addition, the results reach accuracy and repeatability values of ± 2% of full scale providing reliable results with very low bias. Analytical profiles may be adapted to reach concentrations as low as 10 ppb following a continuous sample injection style.

Conclusion

Dry colorimetric detection offers an analytical solution for sulphur determination in liquid and gas hydrocarbons. Apart from good accuracy and repeatability, the technique meets the sulphur monitoring necessities for quality control purposes at different point of the production line in hydrocarbons and other petroleum based products. Moreover, the technique may be extended to other fields where sulphur or hydrogen sulphide need to be monitored and the detection in gas phase are viable.

References

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