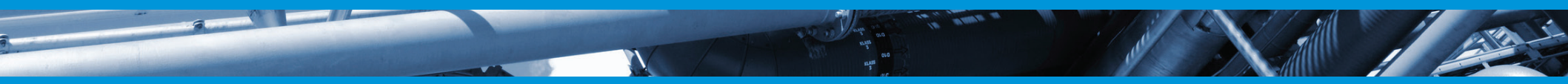
SULFUR MONITORING IN OIL REFINERIES PRODUCTS



Sulfur is one of the most abundant non-metal elements used in a variety of industrial applications, including the production of sulfuric acid, explosives, rubber, fertilisers, pigments, dyes, insecticides, detergents, as well as many inorganic salts and esters production. Sulfur is equally present in petroleum at concentrations ranging between 0.05 to 14wt%. Given the fact that sulfur is naturally found in petroleum products, it is considered an undesired impurity since sulfur 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 sulfur concentration at different stages of hydrocarbon production, it is necessary to identify the critical point during the desulfurisation steps using appropriate analytical methods. Dry colorimetric method provides an option for sulfur 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].

Sulfur, oxygen, nitrogen and some metals compounds are grouped in the hetero atoms commonly found in petroleum products. Sulfur in crude oils is present in the form of organosulfur compounds as mercaptans, mono-and disulfides with alkyl radical chains and thiophenes. Mono- and disulfides are not corrosive in contrast to mercaptans. In spite of a wide variety of organic sulfur compounds, hydrogen sulfide (H_2S) is the predominant inorganic sulfur 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, sulfur oxides (SO_X) may be formed during combustion and they constitute a relevant environmental concern because they are considered air pollutants.

Elemental sulfur 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 sulfur recovery near 99.8% in order to comply with the sulfur 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 sulfur content to 30-50 ppm in gasoline and diesel since January 2005. In fact, the zero-emission or ultra-low sulfur levels in fuels are expected. Desulfurisation technologies and critical point monitoring is mandatory to achieve the ultra-low sulfur content [4]. In addition, sulfur 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].

Testing methods for sulfur in petroleum products

There is a wide variety of analytical techniques available for hydrogen sulfide, total sulfur and specific sulfur speciation (mercaptans and thiols). The choice of the method depends on particular analytical parameters such as the sample phase, matrix composition, detection limit, accuracy, repeatability and reproducibility. It is also worth mentioning that the budget, ease of operation, low maintenance cost and simplicity of the method are also decisive factors in choosing the best technique for the determination of sulfur in petroleum products.

For instance, for hydrogen sulfide determination in petroleum products, there is commercially and automatized qualitative and quantitative methods. In the qualitative category, the doctor test consists in reacting a hydrogen sulfide containing sample with a sodium plumbite solution. A black color appearance indicates the presence of H_2S. The inconvenience of the method lies in the possible interference of mercaptans. About the quantitative H_2S methods in gas and LPG samples, the lead acetate and cadmium sulfide methods are usually applied. For the lead acetate method, a filter paper is chemically impregnated with a lead acetate solution which in contact with H_2S will produce a brown color forming the salt lead sulfide. Methyl mercaptan may produce a transitory yellow stain that fades completely after 5 minutes. The cadmium acetate method consists in reacting a cadmium sulphate acidified solution with the H_2S from the sample. The reaction product is a precipitate that is consecutively titrated with a standard iodine solution.

For the thiol and mercaptans sulfur detection, the doctor test is utilized, once the H_2S has been discarded or removed from the petroleum sample. After applying a qualitative test, then a stain

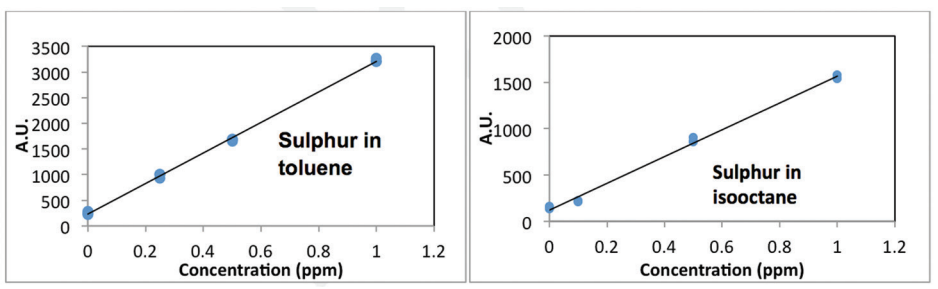


Figure 1: Total sulfur content in different organic solvents at concentration values below 1ppm.

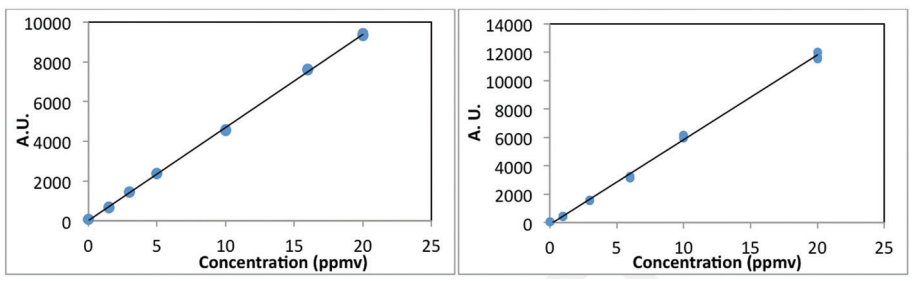


Figure 2: Hydrogen sulfide in nitrogen (left); total sulfur content using COS in nitrogen (right).

tube may use to determine the mercaptans content of a petroleum product sample. The principle of this methodology is based on the length of the stain produced in a detector tube fully packed with a revealing chemical compound. It is a portable device designed for direct and in situ reading from ppb to ppm mercaptans levels in gas samples. In this last category of quantitative tests, we can include the potentiometric method. For this technique, sample is titrated potentiometrically, with a glass electrode as reference and a silver/silver sulfide as indicating electrode, in an alcoholic solution of sodium acetate. Prior to the titration, the H_2S should be removed from the sample; otherwise it would interfere in the results.

The total sulfur content of petroleum products is commonly determine by oxidative pyrolysis in an oxygen rich environment for the sulfur dioxide determination carried out by multiple techniques including oxidative microcoulometry, ultraviolet fluorescence, non-dispersive infrared, x-ray fluorescence spectroscopy, gravimetric and titration methods and even gas chromatography for sulfur speciation [6].

Whether to comply with environmental standards or to control process efficiency under safety practices, it is mandatory to monitor the sulfur 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 sulfur 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 sulfur content is suited for different matrices including gases, LPGs and liquid hydrocarbons at different concentration ranges from low ppb to percentage content of sulfur. 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 sulfur.

Results for total sulfur testing in gases using dry colorimetric method present a linear detector 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 sulfide and carbonyl sulfide in nitrogen. Carbonyl sulfide was measured reducing it to hydrogen sulfide 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 sulfur determination in liquid and gas hydrocarbons. Apart from good accuracy and repeatability, the technique meets the sulfur 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 sulfur or hydrogen sulfide need to be monitored and the detection in gas phase are viable.

References

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Author Contact Details

L. Lorena Torres, C.I. Analytics Corporation • 2085 Boulevard Industriel, Chambly, Quebec J3L 4C5, Canada. • e-mail: info@cianalytics.ca