

Sulphur analysis in aromatic and Naphtha hydrocarbon stream of petroleum products and crude oil

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Nowadays, top priority of petrochemical industries is to detect impurities at extremely low levels to conform to stringent government regulations, protecting expensive catalysts, and ensuring product quality. This article describes and compares different method of analysis to quantify elemental impurities in petrochemical products. Findings revealed that Hydrogenolysis and Rateometric Colorimetry (ASTM 4045) best suits the application requirement of petroleum industry.

Introduction

Crude oil is a complex mixture of different hydrocarbons that varies in appearance and composition depending on the geographical environment. Major constituents in oil, gasoline, diesel, and a variety of solvents are mostly hydrocarbons. Fluid catalytic cracking of petroleum fractions in oil refineries yields three categories of crude oil: paraffinic, naphthenic and aromatic. The mixture can be separated by distillation and gravity. Its composition consists of carbon, hydrogen, sulphur, Nitrogen, oxygen, metals as complexes and salts.

Sulphur is the third most abundant element in crude oil and must be removed due to its corrosive property, intolerable odour and harmful combination to sulphur dioxide (SO₂) and hydrogen sulphide (H₂S). There are two types of crude oil, one that is “sour” containing high amounts of sulphur or sulphur compounds and the second type is “sweet” containing lower sulphur amounts or sulphur compounds. The types of sulphur that can be present in crude oil are sulphides, disulfides, mercaptans, thiophenes, etc.

There is a highly competitive business in petroleum constituents including aromatic hydrocarbons such as (benzene, toluene, ethylbenzene, and xylenes, also known as BTEX), polynuclear aromatic

hydrocarbons (PAH) and Naphthenes. Catalysts used in the Polymerization industry are highly selective and sensitive. These expensive catalysts can be damaged by impurities during the oil refining process. Replacing these catalysts can be very complex, expensive and can eventually lead to loss in business. Hence, impurity analysis has become crucial in this industry. Manufacturers must be able to accurately detect and measure sulphur impurities at very low levels to aid in detecting problems before they occur.

Sulphur measurement as an impurity in hydrocarbon streams

Numerous methods can be used for the determination of sulphur concentration in hydrocarbon stream, but very few are cost and quality efficient. Over the last few decades, many methods were developed for this purpose but not all were effective. For example, lamp combustion and wet chemistry is a labour intensive technique that is only used for liquefied petroleum gas (LPG). The oxidative method and microcoulometry processes also lead to poor precision. Currently, online and test laboratories still using the microcoulometry detection technique are seeking for change because it is labour and time consuming. The cell needs to be frequently cleaned during analysis and chemical solutions must be properly prepared and disposed. Microcoulometry detector is now being replaced by dry colorimetric detector because this technology is simple to use and does not involve wet chemistry. The following techniques are generally used to detect impurities in aromatic compounds in crude oil and petroleum products in laboratories and online application.



❖ Wavelength dispersive X-ray fluorescence, WDXRF

Another method used for the elemental analysis in petroleum products is wavelength dispersive X-ray fluorescence to determine total amount of sulphur in petroleum products. This technique is sensitive and selective for elemental analysis. All the elements in the sample are excited simultaneously and the energy radiations emitted from the compound are diffracted on the monochromator. An analyzing crystal is used to disperse the intensity of emitted photons by diffraction on to the detector. The wavelength intensities are collected by a computer system that is then compared to a calibration curve. The drawback of a WDXRF system is that it requires a high-power X-ray tube in a complicated system. This instrument is very expensive and requires a standard matrix to perfectly match with the sample matrix since carbon and hydrogen ratio differences or other interfering species can lead to false results. It is not suited for field testing where bulky samples need to be quickly analyzed. This technique is very good for higher detection limits of elemental analysis and for less bulky samples.

❖ Inductively coupled plasma atomic emission spectrometry, ICP-AES

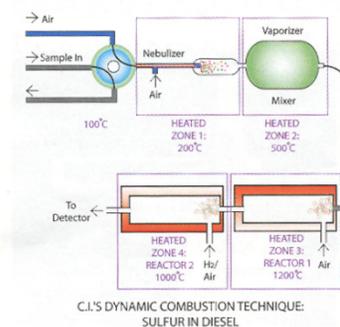
This is a widely used method that implies energy emission of an element at its explicit wavelength i.e., plasma excitation and emission. In this process argon gas is used to avoid combustion at extremely high temperature. This test method is started with samples preparation, and if needed sample is treated with acids, heated or microwave digested. Subsequently, water is excluded from the stream, whereas remaining sample is converted to gaseous phase. A nebulizer is used to convert the liquid sample into aerosol. Upon exposure to about 10,000 degrees Celsius, plasma is excited and the light emission of a specific wavelength is measured. A constant check must be implanted to monitor interferences and corrections must be made instantaneously. Some disadvantages of these instruments are their high cost, viscosity effect and plugging of the nebulizer with particulates. This is a very fast technique for analysis of elements of interest in process solutions as it can measure all elements of interest simultaneously; however, there is a high risk of interference that can falsify result.

❖ High temperature combustion UV-fluorescence

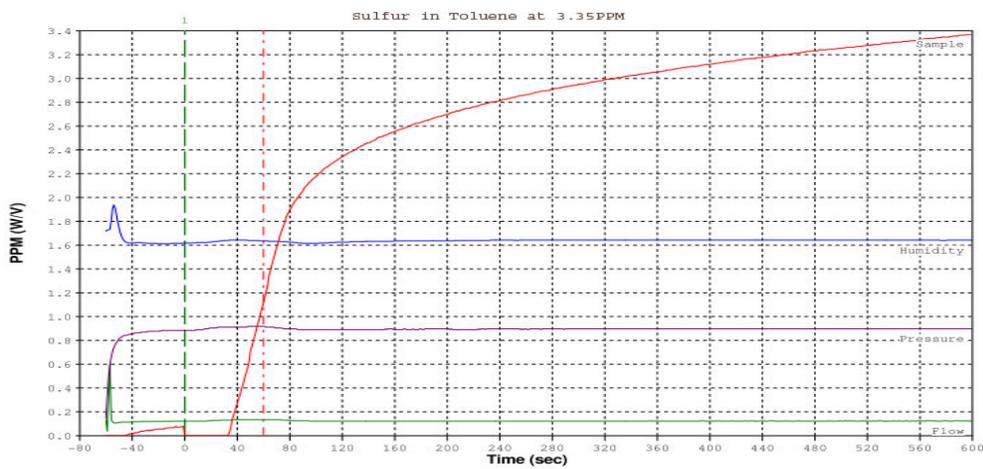
This technique is widely used for diesel blending operations due to its good precision and involves fluorescence spectroscopy. High temperature combustion UV-fluorescence resembles dry colorimetry as both imply combustion of the hydrocarbon stream in the sample and produce CO_2 , H_2O and SO_2 . After the combustion, carbon dioxide and water are removed. The difference between the two methods is that this technique measures SO_2 by ultraviolet fluorescence. As SO_2 enters the reaction cell, it is exposed to ultraviolet radiation. As a result, SO_2 absorbs some of this energy and goes to an excited state. When this molecule returns to its ground state, light is emitted at a particular wavelength. A photomultiplier tube measures the intensity of this light that is directly proportional to the concentration of SO_2 present in the sample. Although this technique measures SO_2 concentrations at low detection levels (PPB), this technique still requires a reference detector because it suffers from U.V. lamp intensity deterioration.

❖ Hydrogenolysis and Rateometric Colorimetry (ASTM D4045)

This method is also known as tape-based, Sensi-tape based or dry colorimetry detector for the determination of sulphur concentration in petroleum products. This is a dry reaction procedure where non-toxic Sensi-tape that is specific to a gas or family of gases reacts and leads to



a measurable color change of the paper. When the Sensi-tape is exposed to the sample a reaction occurs instantaneously and visible results can be observed immediately. This change in color is directly proportional to the concentration of the impurity in the sample stream. The stain on the Sensi-tape is read by a photo-optical system and compared to a calibration curve. This measurement technique is fast, extremely sensitive and exceptionally specific. Tape-detection method detects toxic gases at PPB detection levels. It does not react to other substances found in the process so there is virtually no risk of interference. It is a unique technique that only requires minor change on an analyzer to switch from one impurity to another. It can also be switched from lower PPB detection levels to PPM with minor parameter changes.



Graph 1: Increasing concentration of Sulfur in Toluene (3.35PPM). Dry colorimetry method was used to analyze sulphur concentration in toluene. The theoretical concentration of the sulphur was 3.35ppm and the Analyzer 2010L determined 3.37ppm.

Humidity, pressure and flow are kept constant during the analysis of toluene while organically bound sulphur in hydrocarbon stream sample (including aromatics, naphtha and polynuclear aromatic

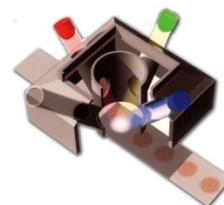


hydrocarbons) is introduced to the reaction tube where it is converted to Hydrogen sulphide (H_2S). This gaseous sample reacts with the specific H_2S Sensi-Tape and as a result a chemical reaction happens on the paper leading to a visible stain. As clearly indicated by ASTM method D4045 the concentration of H_2S measured by this method excludes all interference from other sources which is extremely important during the analyses of complex hydrocarbons mixture.

Two available methods are used to obtain H₂S from an organic hydrocarbon mix:

- ❖ Reductive pyrolysis: Reaction occurs between excess hydrogen and organically bound sulphur in a mixture of hydrocarbon stream at high temperature, products such as H₂S and methane are obtained.
- ❖ Oxidation and reductive pyrolysis: Reaction between air and organically bound sulphur in a mixture of hydrocarbon stream at high temperature generates products such as SO₂, SO₃, CO₂ and H₂O. In the second part of this reaction SO₂, SO₃ are exposed to hydrogen thereby H₂S is obtained. This method helps prevent coking problem.

Dry Colorimetric techniques can analyze liquid, solids or gas samples. This analytical method may also be used as a quality-control tool for sulphur determination in laboratory, process and in finished products. It is a safe technique for workers and requires very low maintenance. Dry Colorimetric technique is based on simple chemistry, there are no known interferences and it has excellent sensitivity at extremely low detection limits.



Conclusion

All of the above test methods are suitable for analysis of sulphur in aromatic and naphtha hydrocarbon stream. There are few differences between these techniques that suit more or less the type of analysis one wants to accomplish. These expensive instruments must be purchased very carefully. Wavelength dispersive X-ray fluorescence (WDXRF) is mostly suited for high detection limits and requires high quality standard preparation. Inductively coupled plasma atomic emission spectrometry (ICP-AES) provides fast results though it suffers from interference and viscosity effect. High temperature combustion UV-fluorescence is a good technique for this type of analysis if its U.V. lamp deterioration problem can be overcome by adding a reference detector. Hydrogenolysis and Rateometric Colorimetry is a unique method that is practically free from interference and maintenance problem. This method suits both laboratory and process analysis and can measure at ultra low PPB levels. All instruments presented above are subject to specifications regarding the application where they are used. Analyzer selection must be made according to the application it will be serving.