

SULFUR COMPOUNDS IN PETROLEUM HYDROCARBON STREAMS

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Abstract

Determination of concentrations of sulfur compounds in different petroleum samples is a true analytical challenge. Only analytical procedures based on gas chromatography can meet the sensitivity and accuracy requirements dictated by up-to-date petroleum industry.

The objective of this work is to develop the method for the quantifying of sulfur compounds in petroleum hydrocarbon streams. The optimum parameters for the GC-SCD method are found in order to determine of sulfur compounds in petroleum fractions. The present study is limited to fractions with final boiling point up to 100°C from the refining unit. Twelve petroleum samples are analyzed. The total sulfur contents of these samples are determined by GC-SCD and UV fluorescence detection. The data obtained are agreement.

Key words: sulfur compounds; GC-SCD; UV fluorescence detection; petroleum hydrocarbon streams.

1. Introduction

There are many reasons for the considerable interest that is focused on determining sulfur compounds. In petrochemical sulfur compounds are of concern because they poison catalysts and cause corrosion. In particular, thiols, sulfides and disulfides are toxic and therefore potentially harmful to humans and even trace levels of these substances give rise to odor problems that constitute an important public health issue.

Numerous difficulties are associated with analyses for sulfur compounds, since they can occur in very complex matrices and often in widely varying concentrations. Moreover, they are highly reactive and have absorptive, adsorptive, photooxidative and metal catalytic properties [1, 2].

Many approaches are proposed to carry out a selective detailed analysis of sulfur compounds in petroleum samples. Gas chromatographs equipped with specific detectors are widely used for the quantitative analysis of sulfur compounds. Gas chromatographic detectors available for the selective determination of sulfur compounds often use the optical intensity of characteristic emission line as their sensing property. The atomic emission detector (AED) utilizes the characteristic sulfur atom lines, but the flame photometric detector (FPD) and the sulfur chemiluminescence detector (SCD) focus on some molecular emission lines of sulfur-containing molecules produced by chemical reactions involving the effluent [3-5]. The SCD is known as an excellent device for sulfur compound analysis. Many laboratories have worked with this detector. In comparison to the other detectors, hydrocarbon interferences are negligible and it has an equimolar sulfur response [6].

In this report, we demonstrate a fast method for the analysis of sulfur compounds in petroleum fractions. In this work, we try to assess the content the individual sulfur compounds in petroleum hydrocarbon fractions based on gas chromatographic analysis with sulfur selective detection.

2. Experimental

2.1 Reagents and samples

Merck and Fluka analytical grade reagents are used. SCD certified standard of sulfur compounds is purchased from Supelco Inc (Agilent Part Number G2933-85001). The certified organic standard, tri-element (ERT-037, Tekmar part number 511-945) containing sulfur ($100.7 \pm 0.6 \text{ ng} \cdot \mu\text{L}^{-1}$) is obtained from Cerilliant Corporation, TX, USA. The standards are used for optimization of sulfur detector selectivity.

Light petroleum hydrocarbon streams samples are produced of Loukoil Neftochim Bourgas JSC, Bulgaria.

2.2 GC-SCD analysis

The gas chromatograph is a model 7890A coupled to a sulfur chemiluminescence detector series model 355 (Agilent Technologies, Inc., USA). A 30 m HP-1 capillary column 320 μm id with 4 μm film thickness is used. The GC separation is performed under the following conditions: helium as carrier gas, column temperature programmed from 50°C 4 min to 120°C at a rate of 20°C.min⁻¹, hold 4 min and to 220°C at a rate of 10°C.min⁻¹, hold 4 min. Injector in split mode at a temperature of 240°C (split vent 131.7 ml.min⁻¹, column 2.6 ml.min⁻¹, purge vent 3 ml.min⁻¹, split ratio 50:1) is used. The SCD detector is set to the following conditions: burner temperature 800°C, vacuum of burner 370 torr, vacuum of reaction cell 7 torr, hydrogen 40 ml.min⁻¹, air 60 ml.min⁻¹. The injection volume is 1.0 μL .

2.3. GC-MS analysis

GC-MS analysis is performed on a model 7890A gas chromatograph equipped with model 5975C Inert XL EI/CI mass selective detector (Agilent Technologies, Inc., USA). Analytes are separated with a PONA (Cross linked Methyl Silicone Gum) capillary column, 50 length m \times 199 μm id \times 0.5 μm film thickness. The column temperature program is as follows: held at 35°C for 0 min and then increased at 2°C.min⁻¹ to 200°C. All injections are performed in the split mode, split ratio 60:1. The injector temperature is held at 200°C. The carrier gas is helium at a flow rate of 0.8ml.min⁻¹. When operated in the full-scan mode, masses of 10-300 m/z are monitored and ionization is carried out in the electron ionization (EI) mode. The ion source temperature is maintained at 230°C and the transfer line temperature is 150°C.

2.4 Total sulfur analysis

Elemental Analyzer model Multi EA3100 (Analytik Jena AG, Germany) is used for determining the sulfur content in samples by fluorescence's detection. The aliquot of sample is dosed directly into combustion tube. Argon, high-purity grade is used as carrier gas at a flow rate of 100ml.min⁻¹. There, the sample is subjected to pyrolysis in the stream of argon. Oxygen, high-purity grade is used for oxi-combustion and ozone generation. The gases from the pyrolysis are completely oxidised in the stream of oxygen (300ml.min⁻¹). The furnace oxidative temperature is kept at 1050°C. The gas to be analysed is dried and then passes to the reaction chamber of the UV fluorescence detector. The wavelength with is used to excite the SO₂ molecules with the UV fluorescence detector is 220 nm.

3. Results and discussion

The gas chromatographic method is developed to enable determination of the concentration of sulfur compounds in light hydrocarbon fractions and methyl tertiary-butyl ether. Sulfur compounds existing in these samples are very involved analytes. The volatility, polarity and reactivity of the sulfur compounds logically lead to the choice of a non polar thick-film column for their separation. The main stationary phases used for separation of sulfur compounds are non polar phases based on polydimethylsiloxanes. A column with a low phase ratio will give sufficient retention to the volatile sulfur compounds. A HP-1 column's phase ratio is 20 and the column gives satisfactory separations of sulfur compounds in investigated samples [7].

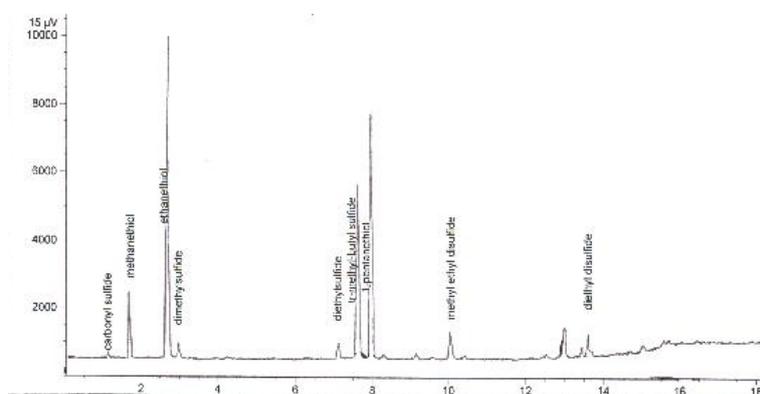


Figure1. Gas chromatogram of the sulfur compounds in the methyl tertiary-butyl ether sample.

Figure 1 shows a chromatogram of the sulfur compounds in methyl tertiary-butyl ether. It can be concluded that the column is the best choice for the separation of sulfur compounds and gives good peak shapes for all compounds of interest.

For this purpose the experimental conditions are varied systematically. The sulfur containing compounds are identified by comparison of their retention times with those of reference standards and by gas chromatography-mass spectrometry (Table 1).

Table 1. Sulfur compounds identification

| Nº | Compound | Retention time, min | Ion m/z (relative abundance) | Other ions m/z |
|-----|----------------------------|---------------------|--------------------------------|------------------|
| 1. | Hydrogen sulfide | 1.018 | 34 (100%) | 32, 33, 36, 35 |
| 2. | Carbonyl sulfide | 1.115 | 60 (100%) | 32, 28, 44, 62 |
| 3. | Methanethiol | 1.704 | 47 (100%) | 48, 45, 46, 50 |
| 4. | Ethanethiol | 2.699 | 62 (100%) | 29, 47, 27, 28 |
| 5. | Dimethyl sulfide | 3.004 | 62 (100%) | 47, 45, 46, 61 |
| 6. | Carbon disulfide | 3.494 | 76 (100%) | 44, 32, 78, 38 |
| 7. | 2-Propanethiol | 3.844 | 43 (100%) | 27, 76, 61, 27 |
| 8. | 2-Methyl-2-propanethiol | 4.838 | 57 (100%) | 41, 90, 29, 75, |
| 9. | 1-Propanethiol | 5.157 | 43 (100%) | 27, 76, 61, 27 |
| 10. | Methyl-ethyl sulfide | 5.294 | 61 (100%) | 76, 48, 47, 27 |
| 11. | 2-Methyl-1-propanethiol | 6.632 | 57 (100%) | 41, 90, 29, 75 |
| 12. | Diethyl sulfide | 7.391 | 90 (100%) | 47, 75, 62, 61 |
| 13. | tert-Methyl-buthyl sulfide | 7.683 | 61 (100%) | 56, 41, 104, 27 |
| 14. | 1-Pentanethiol | 9.548 | 42 (100%) | 55, 41, 70, 104 |
| 15. | Methyl-ethyl-disulfide | 10.054 | 80 (100%) | 108, 29, 27, 45 |
| 16. | Diethyl disulfide | 13.605 | 122 (100%) | 66, 29, 94, 27 |

Equimolar response of a detector refers to the property of the detector that yields equal responses to equal amounts of analytes on a molar basis. This property is a direct consequence of the conversion step employed in SCD. Relying on the equimolarity of the SCD, one can determine the mass of sulfur present in the sample. This is reasonably the most important characteristic of the chemiluminescence detector because it allows the detector to quantitative the sulfur content of each analyte present in the sample with a single standard calibration. The GC-SCD is calibrated with a SCD certified standard of sulfur compounds. In order to establish its linear response and its detection limits, SCD certified standard of sulfur compounds with various sulfur contents from 13 to 56 ppm are analyzed. Quantitative results are obtained from measured areas sulfur compounds peaks. The quantification of each peak of SCD certified standard is used as data to determine the calibration curves. The amount of each compound is obtained by correcting the GC-SCD data by the molecular weight of the molecule, number of sulfur atomic and atomic weight of sulfur. It can be noticed that the calibration coefficients are different and they are of the same order of magnitude for sulfide and thiophene type compounds.

Direct chromatographic analysis of sulfur compounds is favoured because it can reduce the analysis time by eliminating time-consuming procedures of samples preparation, which can additionally cause contamination or loss of analytes. The developed method is applied to the analysis of several light hydrocarbon streams and methyl tertiary-butyl ether samples. The fractions are obtained from two different technology installations. Results from samples analysis are summarized in Tables 2 and 3.

Detector stability and precision are measured over one week period by tracking the total sulfur measured in a sample of the petroleum product and the calibration standard. The variation in the total sulfur response over the period studied is 3 % relative. Accuracy is evaluated by comparing of total sulfur results from the analysis of ten samples with total sulfur as determined by UV fluorescence detection [8]. Results of this comparison are summarized in Table 4. It is apparent that values from the proposed method and the reference method are comparable for analysis of samples.

Table 2. Sulfur compounds contents (in ppm) in methyl tertiary-butyl ether samples

| Compound | MTBE-sample 1 | MTBE-sample 2 | MTBE-sample 3 | MTBE-sample 4 | MTBE-sample 5 | MTBE-sample 6 | MTBE-sample 7 | MTBE-sample 8 |
|----------------------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| Carbonyl sulfide, | 1.8 | 3.0 | 0.1 | 0.3 | 0.6 | 0.2 | nd | 0.3 |
| Methanethiol | 2.0 | 2.3 | 2.1 | 2.7 | 2.1 | 3.7 | 23.7 | 3.3 |
| Ethanethiol | 3.5 | 20.0 | 25.9 | 24.8 | 21.4 | 28.7 | 252.3 | 22.4 |
| Dimethyl sulfide | 2.0 | 2.3 | 1.3 | 1.2 | 1.2 | 1.5 | 15.1 | 1.2 |
| 2-Methyl-2-propanethiol, | nd | nd | nd | nd | nd | nd | 0.7 | 0.2 |
| Carbon disulfide | 18.0 | 3.8 | nd | nd | nd | nd | nd | nd |
| Diethyl sulfide | 1.9 | 1.7 | 1.1 | 0.4 | 0.6 | 0.7 | 7.0 | 0.5 |
| tert-Methyl-buthyl sulfide | 3.1 | 8.9 | 7.7 | 7.9 | 6.1 | 8.2 | 98.9 | 11.2 |
| Dimethyl disulfide | 25.5 | 27.7 | 12.7 | 8.0 | 13.2 | 9.5 | 43.8 | 9.0 |
| Methyl-ethyl-disulfide | 6.0 | 5.6 | 2.5 | 1.7 | 2.4 | 1.5 | 50.5 | 2.6 |
| Diethyl disulfide | 9.5 | 7.6 | 1.9 | nd | 4.3 | 0.9 | 50.0 | 2.5 |

Table 3. Content of sulfur compounds in C₄-hydrocarbon fractions samples

| Compound | Samples | | | |
|--------------------------|---------------------------|--------------|------------------|------------------------------|
| | Feed to caustic wash, ppm | Top DIB, ppm | Bottoms DIB, ppm | Effluent caustic to DIB, ppm |
| Methanethiol | 15 | 22 | <1 | <1 |
| Ethanethiol | 124 | 84 | 293 | <1 |
| 1-Propanethiol | 2 | <1 | 8 | <1 |
| 2-Propanethiol | 24 | <1 | 83 | <1 |
| 2-Methyl-2-propanethiol | 1 | <1 | 4 | <1 |
| 2-Methyl-1-propanethiol | 3 | <1 | 11 | <1 |
| Dimethyl sulfide | 16 | 8 | 40 | 5 |
| Methyl-ethyl sulfide | 6 | <1 | 18 | <1 |
| Carbon disulfide | 2 | <1 | 3 | <1 |
| Dimethyl disulfide | 1 | 3 | <1 | 3 |
| Methyl-ethyl-disulfide | 2 | 3 | <1 | 5 |
| Diethyl disulfide | 1 | 2 | 13 | 4 |
| Unknown sulfur compounds | | 3 | 33 | |

Table 4. Determination of sulfur content in different petroleum hydrocarbon fractions

| Samples | Sulfur content, ppm | |
|-----------------------------------|---------------------|------------------------|
| | Method developed | UV fluorescence method |
| MTBE-sample 1 | 81.5 | 79.4 |
| MTBE-sample 2 | 79.9 | 60.0 |
| MTBE-sample 3 | 55.2 | 62.0 |
| MTBE-sample 4 | 46.7 | 42.0 |
| MTBE-sample 5 | 51.3 | 56.0 |
| MTBE-sample 6 | 54.7 | 48.0 |
| MTBE-sample 7 | 54.2 | 50.0 |
| MTBE-sample 8 | 53.2 | 59.0 |
| Feed to caustic wash installation | 197 | 190 |
| Top DIB | 125 | 138 |
| Bottoms DIB | 506 | 480 |
| Effluent caustic to DIB | 17 | 23.4 |

4. Conclusion

A method is developed for the simultaneous determination of sixteen sulfur compounds in petroleum hydrocarbon stream samples. Our results show that the development method is well suited for analyzing petroleum hydrocarbon samples for sulfur compounds with a broad range of boiling points. A detailed identification and quantitative compound analysis is

carried out using GC-SCD. The development of the method and comparison of results between GC-SCD and UV fluorescence detector are presented. The method is an important tool for the study of the effect of caustic wash conditions on the production of sulfur in petroleum hydrocarbon streams.

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