

Determination and influence factors of total sulphur in diesel fuel by tube furnace combustion-ion chromatography

Shuo Wang^{1,2,3,*}, Weiyu Duan^{1,2,3}, Peng Du^{1,2,3} and Lianqiang Qiu^{1,2,3},
Huanming Lv^{1,2,3} and Zhaojun Qiu^{1,2,3}

¹LiaoNing Inspection Institute of Product Quality Supervision, Shenyang 110144, China

²National Center of Petroleum Quality Supervision Inspection (Shen Yang), Shenyang 110144, China

³Liaoning province industrial lubricating oil monitoring engineering laboratory, Shenyang 110144, China

*Corresponding author e-mail: sekiwangedward@163.com

Abstract. To establish an analytical method for the determination of the trace sulfur in diesel fuel by tube furnace combustion-ion chromatography. Samples were burned through tubular furnace and oxidation of sulfur into sulfate ion in absorbent, which was measured by ion chromatography. The response was linear ($r > 0.9995$) in the range of 0.01 to 5.00mg/L and the limit of detection for the sulfate ion was 0.002mg/L. The application result showed that the recovery rate was higher than 95% and this validated method was successfully applied for the analysis of sulfur in diesel fuel.

1. Introduction

In the modern world, the scientific technique advances and the world economy is rapidly developed, which also lead to irreversible destruction to environment, such as the environmental pollution and the spread of acid rain. The major pollution of sulphur in atmosphere are sulphur dioxide and sulphur trioxide [1]. The world's anthropogenic emissions of sulfur dioxide are estimated about 150 million tons per year, in which more than 70% comes from fuel combustion. Now, the content of sulfur in diesel fuel should be no more than 10mg/kg and the arbitration detection method is UV fluorescence method (GB/T 0689-2000). But in recent years, there has been a large deviation of sulfur content detection results, especially for sulfur content not more than 10mg/kg. Oxygen, chlorine, nitrogen and other elements in samples may be interfere with the determination of sulfur content, or even get a incorrect test results [2]. The purpose of this paper is to establish an analytical method for the determination of sulfur in diesel fuels by tube furnace combustion-ion chromatography [3~6]. This method can effectively avoid the interference of other elements, with low limit of detection and the result is accurate and reliable. Hence, it is a practical method to determine the sulfur content in diesel fuels, which provides technical support for the quality control of diesel fuels.



2. Experiment

2.1. Instrumentation

Our research was carried out using high temperature combustion at 950°C of the diesel fuels in the pure oxygen (99.99%) flow in TSY-1121 sulfur analyzer (tubular furnace method). Oxygen flow rate was 350 ml/min. The diesel fuels were put into the porcelain boats which were introduced into the high temperature zone of the analyzer in the oxygen flow. The combustion products were absorbed in the absorber filled with deionized water and hydrogen peroxide with a concentration of 0.6% (v/v). The absorber liquid volume solution was 2ml. The solution was analyzed using ion chromatograph "ICS-90" (DIONEX). The separation of SO_4^{2-} anion and its detection in water solution and in the absorbate of combustion products containing the same anions was investigated using separation Anion columns "IonPac AS18" (DIONEX) and eluent 10 mmol/L KOH. The analysis was carried at 30°C. The eluent flow rate was 1 mL/min. The sample loop of 20 μl was used for calibration of the ion chromatograph, using prepared standard solution of SO_4^{2-} anion.

2.2. Chemicals

The sulfate anion (1000mg/L, National Institute of Metrology, batch No: GBW (E) 080266) was used for the preparation of the Standard solution and the deionized water (specific resistance 18.2 M Ω) from ultrapure water (integral 15, MILLIPORE) was used for the preparation of all aqueous solutions. Standard substance for the determination of sulfur was purchased from China Petroleum Chemical Co Petrochemical Research Institute (1.0mg/L, 2.0mg/L and 10.0mg/L, batch No: 201606).

2.3. Compounds

All studied diesel fuels were bought in glass bottle and purchased from Petro China Co Ltd. and Sinopec Group in Liaoning province.

2.4. Sample pretreatment

The cleaned porcelain boats and fine sand were calcined for 30min at 950°C and moved to the dryer. The diesel sample was accurately weighed about 15.0mg by the injection needle and coat it on the bottom of the porcelain boat, which was presented as slender strip and covered with fine sand to adsorption of the sample. In the collection tube of the tubular resistance furnace, about 1.5ml of solution of hydrogen peroxide with a concentration of 0.6% (v/v) was added as the absorption liquid, and the exhaust pipe outlet was inserted into the subsurface of the absorbent. Oxygen with flow rate of 350 ml/min and the furnace temperature is set to 950 °C. The porcelain boat gradually moved to the middle part of the tubular resistance furnace. The combustion time was 40min. The exhaust pipe carefully cleaned with ultrapure water and diluted to 2ml. The concentration of sulfate ion in the sample was determined by ion chromatography and the content of sulfur in diesel fuel was calculated.

3. Result and discussion

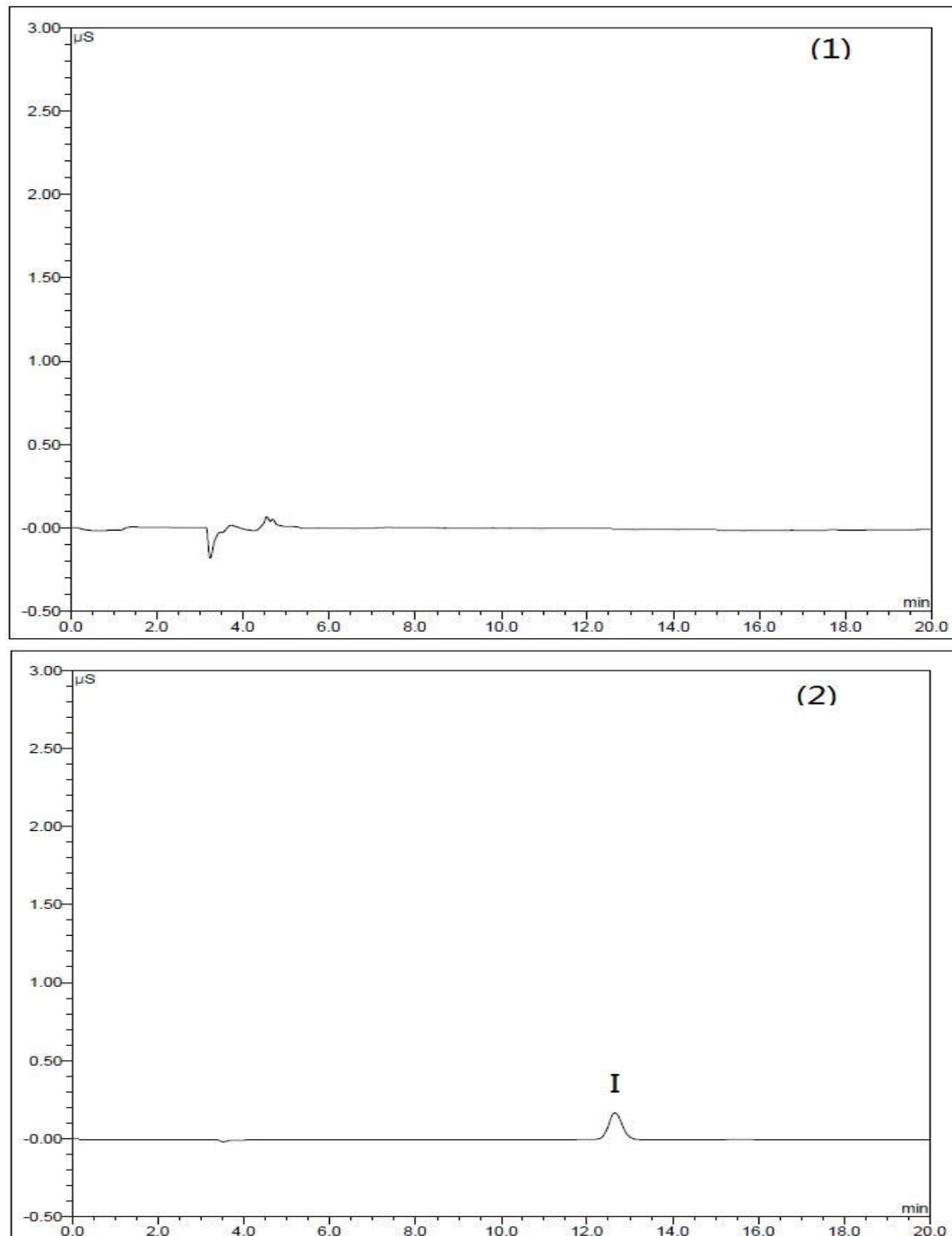
3.1. The maximum sample weight and the oxidizability of hydrogen peroxide

The samples overloaded in porcelain boat can bring errors for incomplete combustion. Under the conditions of this method, loading less than 20mg can be fully combustion. The sulfur dioxide in the combustion of diesel fuel need to react with hydrogen peroxide and be converted to sulfur trioxide. The sulfur dioxide in the combustion could be fully converted to sulfur trioxide at the level of 0.6% (V/V) which met the requirement of this experiment.

3.2. Specificity

The absorbent of samples were analyzed by ion chromatograph. Under this condition, other components have no interference with the determination of sulfate ion and the the oretical plate

number calculated according to the sulfate ion is more than 2000, the retention time is about 12 min. The chromatogram of sulfate ion in diesel fuel can be obtained in Fig.1. The degree of separation between sulfate ion and adjacent peak is more than 1.5.



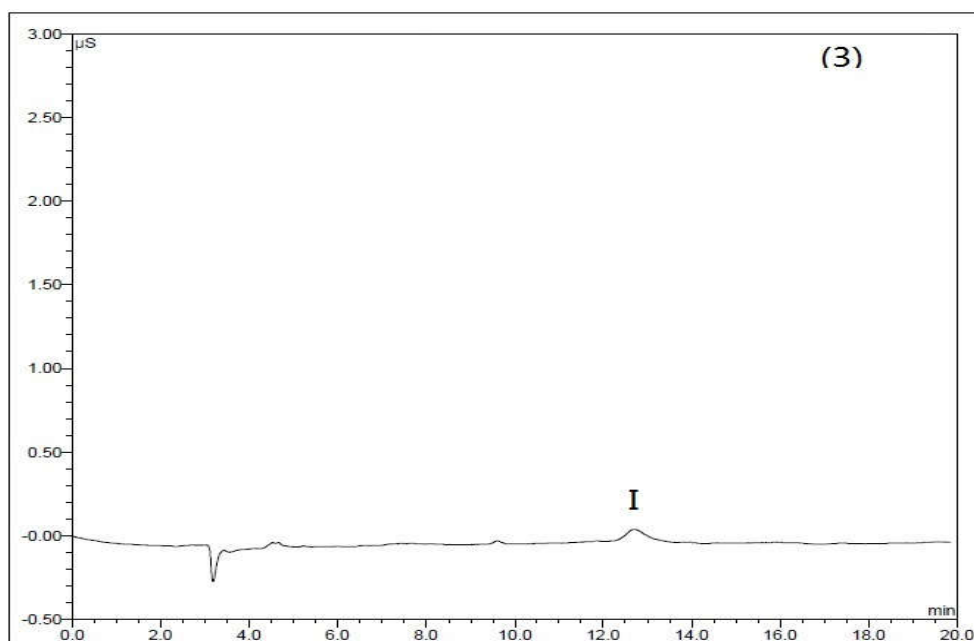


Figure 1. Typical ion chromatogram of blank solution (1), SO_4^{2-} reference solution (2), diesel fuel solution (3). (I. SO_4^{2-})

3.3. Linearity

By the application of external standard method for quantification, the standard solution of 0.01, 0.10, 0.50, 1.00, 2.50 and 5.00 mg/L are injected into ion chromatograph, the sulfate ion chromatographic peak area was measured by ion chromatography, in which peak area (A) as the vertical coordinates and mass concentration (C) (mg/L) as the transverse coordinates, the standard curve equation was drawn. The standard curve equation is $A = 3.0508C + 0.0369$, the correlation coefficient is 0.9998, and the calibration graph was linear within 0.01~5.00 mg/L.

3.4. Limits of detection and quantification

The limits of detection (LOD) and quantification (LOQ) were calculated on the basis of the concentration giving a signal of three and ten times to background noise at the corresponding retention time of sulfur. The evaluation was carried out by analyzing the diluted solutions that contained SO_4^{2-} in below and above the limited values. The LOD and LOQ for sulfate ion are 0.002 mg/L and 0.006 mg/L, respectively. The proposed methodology fully meets the requirements of relational directives.

3.5. Precision, reproducibility and recovery

Certified reference material of diesel fuel containing sulfur was employed to validation the precision and accuracy of the developed method. The standardized products solution with 0.10 mg/L sulfate ion, according to the chromatographic conditions and after 6 times of repeated injection, the peak area was measured and the degree of precision was calculated. As another important criterion of the precision, the reproducibility of the methods was evaluated by repetitious analysis of the sulfate ion standard. The results showed that the precision and reproducibility meet the requirements of relational directives, which RSD% was 4.22% and 4.98%.

The standard substances for sulfur determination (1.0 mg/L, 2.0 mg/L, 10.0 mg/L) were employed to validation the recovery. Each of samples were pretreated and analyzed in triplicate under the established method, as described previously. The results show that the recoveries varied between 92.90% and 99.26% for sulfur (RSD% less than 5%). The result of recovery rate can be obtained in table 1.

Table 1. Recovery rates of sulfur in diesel fuel

Marked amount (mg/L)	measured value (mg/L)	Recovery rate (%)	The average recovery rate (%)	RSD (%)
1.0	0.949	94.90	95.47	3.03
1.0	0.986	98.60		
1.0	0.929	92.90		
2.0	1.917	95.85	96.92	1.52
2.0	1.926	96.30		
2.0	1.972	98.60		
10.0	9.624	96.24	97.94	1.58
10.0	9.833	98.33		
10.0	9.926	99.26		

4. Conclusion

The combination of tube furnace combustion and ion chromatography appeared to produce a reliable and simple method for determination of trace sulfur in diesel fuel. The procedure is efficient and easy to handle. In combination, Ion chromatography is the most convenient and sensitive method for detection of sulfur and can effectively avoid the interference of other elements. Furthermore, this method was validated for linearity, LOD, precision, accuracy and recovery rate. In conclusion, this rapid and versatile method is suitable for quantitative analysis and quality control of diesel fuel.

Acknowledgments

The authors thank the Key Program of Liaoning provincial Natural Science Foundation of China (No. 20170520108) and the Liaoning provincial Natural Science Foundation of China (No. 20170520108) for supporting this research.

References

- [1] Mrd S. Lichens and sulphur dioxide air pollution: field studies [J]. *Environmental Reviews*, 1993, 1 (2):73-91W. Strunk Jr., E.B. White, *The Elements of Style*, third ed., Macmillan, New York, 1979.
- [2] He F, Zhe XL, Zheng L, et al. Determination of Total Sulfur Content in Light Oil Products by Ultraviolet Fluorescence Spectrometry [J]. *Chin Petrol Processing Petrochem Technol*, 2017, 48 (9): 97-102.
- [3] Kinani A, SaLhi H, Bouchonnet S, et al. Determination of adsorbable organic halogens in surface water samples by combustion–microcoulometry versus combustion–ion chromatography titration [J]. *Journal of Chromatography A*, 2018, 1539: 41-52.
- [4] Nagashima H, Dewa Y. Rapid and Simultaneous Micro-analysis of Halogens and Sulfur in Organic Compounds by Combustion - Ion Chromatography [J]. *Bunseki Kagaku*, 2017, 66 (2):81-87 American Institute of Physics, Melville, NY, 2002, pp. 651–654.
- [5] Yang Y, Zhong M, University H N. Determination of Fluorine, Nitrogen, Chlorine and Sulfur in Branches, Leaves and Fruits of Mulberry by Oxygen Bomb Combustion Ion Chromatography[J]. *Guangdong Chemical Industry*, 2017, 44 (13): 268-269.
- [6] Junior G S C, Pereira R M, Hartwig C A, et al. Determination of Cl and S in Edible Seaweed by Ion Chromatography after Decomposition by Microwave-induced Combustion[J]. *Revista Virtual De Quimica*, 2017, 9 (2):492-501.