Determination of Total Sulphur and Chloride in Solid Biomass Fuel by Tube Furnace Combustion-Ion Chromatography

Shuo Wang\textsuperscript{1,2,3,*}, Weiyu Duan\textsuperscript{1,2,3}, Cong Cao\textsuperscript{1,2,3}, Zheyuan Yang\textsuperscript{1,2,3}, Huanming Lv\textsuperscript{1,2,3} and Zhaojun Qiu\textsuperscript{1,2,3}

\textsuperscript{1}LiaoNing Inspection Institute of Product Quality Supervision, Shenyang 110144, China
\textsuperscript{2}National Center of Petroleum Quality Supervision Inspection (Shen Yang), Shenyang 110144, China
\textsuperscript{3}Liaoning province industrial lubricating oil monitoring engineering laboratory, Shenyang 110144, China

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

Abstract. A tube furnace combustion-ion chromatography method for the determination of total sulfur and chlorine in biomass solid fuel were established. Taking 0.15\% hydrogen peroxide as absorption liquid, the sulfide of the sample is converted into sulfate ion after combustion. The total sulfur and chlorine content in the biomass solid fuel is determined by ion chromatography. Under the optimized chromatographic conditions, the detection limit of sulfate ion chromatography is 3.1 mg / kg and the detection limit of chlorine is 4.6 mg/kg with the linear relationship in the range of 0.05-10.00 mg/L. The relative standard deviation of precision and repeatability is less than 5\%, the average recovery of total sulfur and chlorine were 97.9\% and 96.6\%. This method is simple, rapid and reproducible. It can be used for the determination of total sulfur and chlorine in biomass solid fuel.

1. Introduction

As a kind of green and renewable resource, solid biomass fuel is increasingly favored and plays an increasingly important role in energy pattern. It usually comes from crop waste, such as branches, shrubs and crop straw, etc. After combustion, the ash of solid biomass fuel is about 10\% of coal, which can greatly reduce the emission of particulate matter in the atmosphere. Solid biomass fuel meet market trend and have a broad application prospect. 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 gas produced by combustion of sulfide and chloride is the main substance of acid rain, which are very important environmental control indicators [1]. At present, the determination of total sulfur content in solid biomass fuel is mainly based on the GB/T 28732-2012 and the determination of total chlorine content is mainly based on the GB/T 30729-2014. These method are complex, time-consuming and may cause deviation of detection results. Tube furnace combustion-ion chromatography is a mature method for the determination of total sulfur and chlorine [2-5]. In this study, total sulfur and chlorine content in
solid biomass fuel were determined by tube furnace combined with ion chromatography. This method can effectively avoid the interference of other elements, and the result is accurate and reliable. Hence, it is a practical method to provide technical support for the quality control.

2. Experiment

2.1. Instrumentation
Our research was carried out at 1050°C in the oxygen (99.99%) flow in TSY-1121 sulfur analyzer. Oxygen flow rate was 400 ml/min. The solid biomass fuels were put into the porcelain boats which were introduced into the high temperature zone of the analyzer. The combustion products were absorbed in the absorber filled with hydrogen peroxide a concentration of 0.15% (v/v). The absorber liquid volume solution was 5mL. The solution was analyzed using ion chromatograph “ICS-90”. The separation of SO$_4^{2-}$, cl$^-$ and its detection in water solution and in absorption solution were investigated using Anion columns “IonPac AS18” (DIONEX) and eluent 12 mmol/L KOH. The analysis was carried at 40°C. The eluent flow rate was 1.0 mL/min. The sample loop of 20 μL.

2.2. Chemicals
The sulfate anion and chloride anion (1000mg/L, National Institute of Metrology, batch No: GBW (E) 080266 and GSB04-1770-2004) were used for the preparation of the Standard solution and the ultrapure water (specific resistance 18.2 MΩ) from Integral 15 (MILLIPORE) was used for the preparation of all aqueous solutions.

2.3. Compounds
All studied solid biomass fuels were prepared by ourselves, which comes from crop straw.

2.4. Sample pretreatment
The cleaned porcelain boats and sand were calcined for 30min at 1050°C before use. solid biomass fuels were accurately weighed about 200mg 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 3.0ml of solution of hydrogen peroxide with a concentration of 0.15% (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 400 ml/min and the furnace temperature is set to 1050 °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 5.0mL. The concentration of sulfate and chloride ion in the sample was determined by ion chromatography and the content of total sulfur and chlorine in sample 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 500mg 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 0.15% (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 target compounds and the the oretical plate number calculated are more than 2000, the retention time of $\text{SO}_4^{2-}$ and cl$^-$ are about 6.2 and 12.7 min.
The chromatogram of sulfate anion and chloride anion in solid biomass fuels can be obtained in Fig.1. The degree of separation between target compounds and adjacent peak is more than 1.5.

![chromatogram](image)

**Figure 1.** Typical ion chromatogram of blank solution (1). SO$_4^{2-}$ and cl$^-$ reference solution (2). solid biomass fuels solution (3).(In which I represents cl$^-$ and II represents SO$_4^{2-}$)

### 3.3. Linearity

By the application of external standard method for quantification, the sulfate anion and chloride anion standard solution of 0.05, 0.10, 0.50, 2.50, 5.00 and 10.00mg/L are injected into ion chromatograph, respectively. The sulfate anion and chloride ion chromatographic peak area were 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 sulfate anion standard curve equation is $A=0.3286C-0.0134$, the correlation coefficient is 0.9998. The chloride anion standard curve equation is $A=0.4962C+0.0252$, the correlation coefficient is 0.9996. The calibration graph of sulfate anion and chloride anion were linear within 0.05~10.00 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 sulfate anion and chloride anion. 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 0.005 mg/L and 0.016 mg/L, respectively. The LOD and LOQ for chloride anion are 0.003 mg/L and 0.010 mg/L, respectively. The proposed methodology fully meets the requirements of relational directives.

### 3.5. Precision, reproducibility and recovery

Certified reference material of solid biomass fuel containing sulfur and chlorine were employed to validation the precision and accuracy of the developed method. The standardized products solution with 0.50mg/L sulfate ion and chloride 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. The reproducibility of this method was evaluated by repetitious analysis of the sulfate ion and chloride ion standard. The results showed that the precision and reproducibility meet the requirements of relational directives, which RSD% was 4.51% and 3.86%. The standard substances for sulfur and chlorine determination (0.5mg/L, 2.0mg/L, 5.0mg/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 of sulfur varied between 94.5% and 99.6% (RSD% less than 5%) and the recoveries of chloride varied between 92.4% and 99.1% (RSD% less than 5%). The result of recovery rate can be obtained in table 1.
Table 1. Recovery rates of sulfate anion and chloride anion in solid biomass fuel

| Marked amount (mg/L) | Measured value (mg/L) | Recovery rate (%) | Average recovery rate (%) | RSD (%) |
|----------------------|-----------------------|-------------------|---------------------------|---------|
|                      |                       | sulfate anion     |                           |         |
| 0.50                 | 0.498                 | 99.6              | 99.1                      | 0.73    |
| 0.50                 | 0.496                 | 99.2              |                           |         |
| 0.50                 | 0.491                 | 98.2              |                           |         |
| 2.00                 | 1.982                 | 99.1              | 97.9                      | 1.43    |
| 2.00                 | 1.927                 | 96.4              |                           |         |
| 2.00                 | 1.964                 | 98.2              |                           |         |
| 5.00                 | 4.833                 | 96.7              | 96.9                      | 2.64    |
| 5.00                 | 4.726                 | 94.5              |                           |         |
| 5.00                 | 4.981                 | 99.6              |                           |         |
|                      |                       | chloride anion    |                           |         |
| 0.50                 | 0.486                 | 97.2              | 95.8                      | 4.06    |
| 0.50                 | 0.494                 | 98.8              |                           |         |
| 0.50                 | 0.457                 | 91.4              |                           |         |
| 2.00                 | 1.969                 | 98.5              | 98.1                      | 1.18    |
| 2.00                 | 1.937                 | 96.9              |                           |         |
| 2.00                 | 1.982                 | 99.1              |                           |         |
| 5.00                 | 4.861                 | 97.2              |                           |         |
| 5.00                 | 4.922                 | 98.4              | 96.0                      | 3.35    |
| 5.00                 | 4.618                 | 92.4              |                           |         |

4. Conclusion
The tube furnace combustion-ion chromatography is a reliable and simple method to determinate trace total sulfur and chlorine in solid biomass fuel. This method is simple and rapid in operation, good linearity of standard working curve, low detection limit, high accuracy and precision. It can avoid the interference of other elements in samples and is suitable for the determination of total sulfur and chlorine content in biomass solid fuel.

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