# APPLICATION NOTE

## Analysis of Chloride and Sulfur in Biodiesel Fuel by CIC

- **Fully Automated Combustion System**
- **Chloride & Sulfur Determination**
- **Sample Versatility**

**Keywords:**
***MultiTek®, pyrohydrolysis, biofuels, halides, Biodiesel Fuel, corrosion, chloride, sulfur, sulfate, combustion ion chromatography (CIC)***

## INTRODUCTION

Renewable fuels such as biodiesel provides alternatives to foreign and domestic fossil fuel consumption and dependency. Biodiesel is commonly blended with other petroleum products, but can be sold and used in pure form. ASTM methods D7467 & D6751 contain specifications on biodiesel blends ranging up to 20%.

Two components that are monitored closely because of their harmful oxides and corrosive acids are sulfur and chloride. Sulfur oxides result from the combustion and emission of sulfur contaminated fuels into the environment. Also, high sulfur content can alter other properties such as ignition point and stability. Chloride in biofuels can be converted into the corrosive acid, hydrochloric acid, which can corrode plant process equipment and engine components.

Total chloride and sulfur compounds in biodiesel fuels can be analyzed in the MultiTek by oxidative pyrohydrolytic combustion followed by ion chromatography conductivity detection. The process starts with pyrohydrolysis of the samples at 1050ºC. In the pyrotube with the help of steam, halogen containing compounds are converted into an acid gas state. Sulfur containing compounds are oxidized to sulfur dioxide ($SO_2$) and in a unequalled occurrence eventually converted to sulfite ($SO_3$) and sulfate ($SO_4$). Once combustion is completed, gases are condensed and absorbed in a solution composed of UHP 18.2 MOhm water and phosphate internal standard. The solution is then transferred by the MultiTek® to an injection system on the Ion Chromatograph (IC) for conductivity analysis.

## REACTIONS

Halogen Reaction

$$R - Cl \xrightarrow[1050℃ + O_2 + H_2O]{} HCl$$

Sulfur Reaction

$$R - S \xrightarrow[1050℃ + O_2 + H_2O]{} SO_x \xrightarrow[scrubber\ solution]{} SO_4$$

To ensure the highest oxidation conversion from sulfite to sulfate, optima grade hydrogen peroxide can be added to the scrubber solution.

## EXPERIMENTAL CONDITIONS

- **Instrumentation**

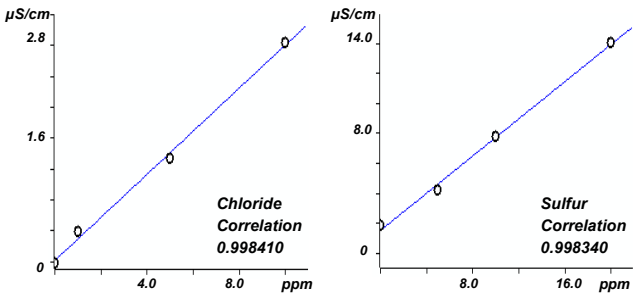
Antek MultiTek Horizontal IC, Antek Model 740 boat inlet system, Antek Model 735 syringe drive, autosampler and suppressed IC system.


- **Instrument Parameters**

| | |
|---|---|
| Injection Volume (µL) | 20 |
| GFC1- Ar/He (mL/min) | 130 |
| GFC2- Pyro $O_2$ (mL/min) | 450 |
| GFC4- Carrier $O_2$ (mL/min) | 30 |
| Furnace (ºC) | 1050 |
| Sample Burn Time (mm:ss) | 4:00 |

# APPLICATION NOTE

- **Standards**




*A four level calibration was made using certified sulfur (dimethyl sulfide) in biodiesel standards spiked with trichloroacetic acid for source of chloride. CIC calibration is performed through entire sample flow path*

- **Limit of Detection**

| | Chloride | Sulfur |
|---|---|---|
| LOD (µg/kg) | 100 | 500 |

***PAC also offers a MultiTek with UVF (ultra-violent florescence) detection and/or a Trace Halides Kit p/n 103310 where lower detection limit can be achieved. Data used for these calculations produced a signal to noise ratio greater than 3:1. Highest quality (+99.9%) reagents, gases and 18.2 MΩ water are required to achieve these LODs.***

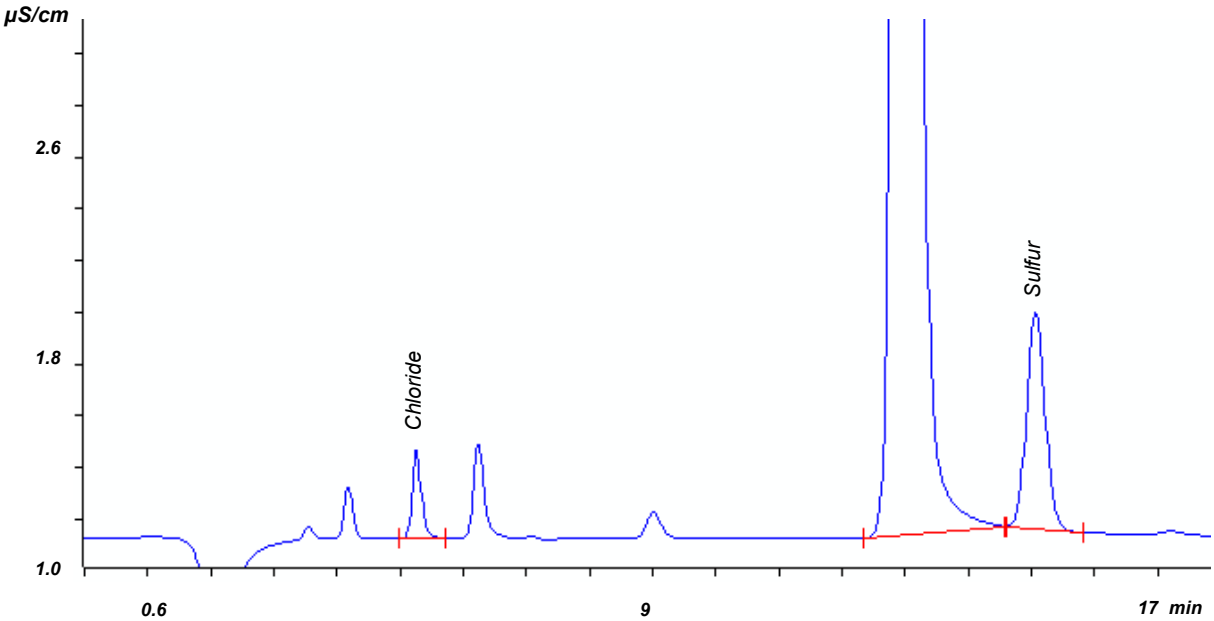
## RESULTS

| Analysis ppm (wt/wt; Cl/S) | Chloride (µg/kg) | Sulfur (µg/kg) |
|---|---|---|
| Biodiesel 1/5 | 1.4 | 4.0 |
| Biodiesel 1/5 | 1.3 | 4.1 |
| Biodiesel 1/5 | 1.3 | 4.3 |
| Biodiesel 5/10 | 4.5 | 9.0 |
| Biodiesel 5/10 | 4.5 | 9.5 |
| Biodiesel 5/10 | 4.7 | 10.0 |
| Biodiesel 10/20 | 10.1 | 18.9 |
| Biodiesel 10/20 | 10.0 | 19.4 |
| Biodiesel 10/20 | 10.1 | 19.3 |
| Unknown | 5.8 | 16.5 |
| Unknown | 5.6 | 15.5 |
| Unknown | 5.5 | 15.9 |
| Average %RSD | 2.5 | 3.1 |

*Results and repeatability of certified biodiesel calibration and unknown sample.*

## CONCLUSION

These results demonstrate that the MultiTek Analyzer equipped with Ion Chromatography provides a sensitive, automated and reliable analysis of chloride and sulfur in biodiesel fuel. This analysis will allow the refinery and blenders to closely monitor concentration levels and meet regulatory requirements.




*Biodiesel Fuel Chromatography*

*Antek's MultiTek is the only instrument on the market that combines sulfur, nitrogen, and halides testing all in one. Compact, powerful, automated, and multi-configurable, it's the perfect solution for today's increasing demand for fast and accurate detection of unwanted chemicals, pollutants, contaminants, and corrosive elements. Because MultiTek delivers precise results with high sensitivity and unmatched versatility, it's a valuable process optimization tool that will deliver faster ROI and a better bottom line.*



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