APPLICATION NOTE

ANTEK by PAC

MultiTek® Halides & Sulfur in Liquefied Petroleum Gas (LPG) by Oxidative Pyrohydrolytic Combustion followed by Ion Chromatography Conductivity Detection

- **Fully Automated Combustion System**
- **Halogen Determination**
- **Sample Versatility**

Keywords:
MultiTek, pyrohydrolysis, halides, liquefied petroleum gas (LPG), n-butane, fluoride, chloride, bromide, sulfur, combustion ion chromatography (CIC)

INTRODUCTION

Hydrofluoric acid alkylation is a common technique for the production of high octane gasoline and LPG fractions such as n-butane and propane. Even though acid settlers and adsorbent beds are used to remove fluoride, traces still manage to make it into the final product that is delivered to the consumer.

Butane is a common feed used in production and can be blended with other compounds to achieve a desired product. When the fluorides, chlorides and sulfur in the butane react, they can produce extremely corrosive acids such as hydrofluoric and hydrochloric acids. As a result, gas leaks can evolve from these corrosive effects and pushes the need to monitor concentrations of halides and sulfur.

This procedure analyzes total halogens and sulfur compounds (F/Cl/Br/SO_4) in liquefied petroleum gases. Specifically n-butane was chosen, but heavier samples such as pentane and hexane are applicable. 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**

$$R - X_{(F^-\ Cl^-\ Br^-)} \xrightarrow[1050℃ + O_2 + H_2O]{} H\ - X_{(F^-\ Cl^-\ Br^-)}$$

- **Sulfur Reaction**

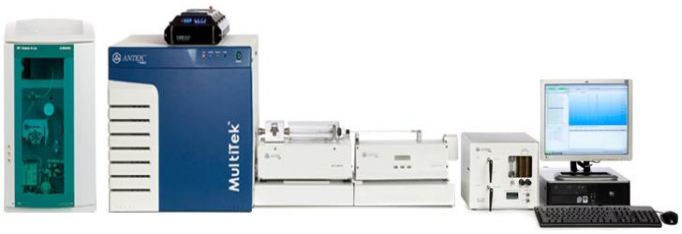
$$R - S \xrightarrow[1050℃ + O_2 + H_2O]{} SO_2 \xrightarrow[scrubber\ solution]{} SO_3^{2-} + SO_4^{2-}$$

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

EXPERIMENTAL CONDITIONS

- **Instrumentation**

Antek MultiTek Horizontal, Antek Model 740 boat inlet system, Antek Model 735 syringe drive, Antek Model 734 Gas/LPG Sampler and suppressed IC system.



- **Instrument Parameters**

734 Sample Loop (µl)	15
IC Sample Loop (µl)	250
GFC1- Ar/He (ml/min)	130
GFC2- Pyro O_2 (ml/min)	450
GFC4- Carrier O_2 (ml/min)	30
734 Carrier- Ar or He (ml/min)	20
Furnace (ºC)	1050
Sample Burn Time (mm:ss)	02:45

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RESULTS

- **Repeatability of ~25 ppm (w/w) n-butane (n=6)**

	Fluoride	Chloride	Bromide	Sulfur
AVG	22.3	24.4	24.8	23.6
STD	0.23	0.57	0.44	1.04
RSD	1.03%	2.33%	1.78%	4.39%

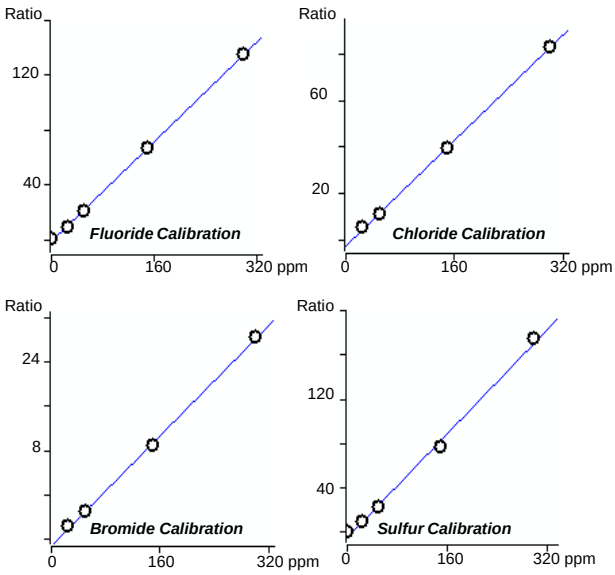
- **Limit of Detection**

	Fluoride	Chloride	Bromide	Sulfur
Limit of Detection	374 ppb	164 ppb	46 ppb	1 ppm

- **Standards**

IC calibration was performed through entire sample flow path using certified n-butane matrix standard materials (0-300ppm). The compounds used for halide addition are fluorobenzene, chlorobenzene, bromobenzene and dimethyl sulfide in n-butane.

- **Calibration**



- **Correlation**

Detection's linearity extends over a dynamic range of 10^3.

0 – 300 ppm	Fluoride	Chloride	Bromide	Sulfur
Correlation Coefficient	0.999	0.999	0.999	0.998
Curve Fit	Linear	Linear	Linear	Linear

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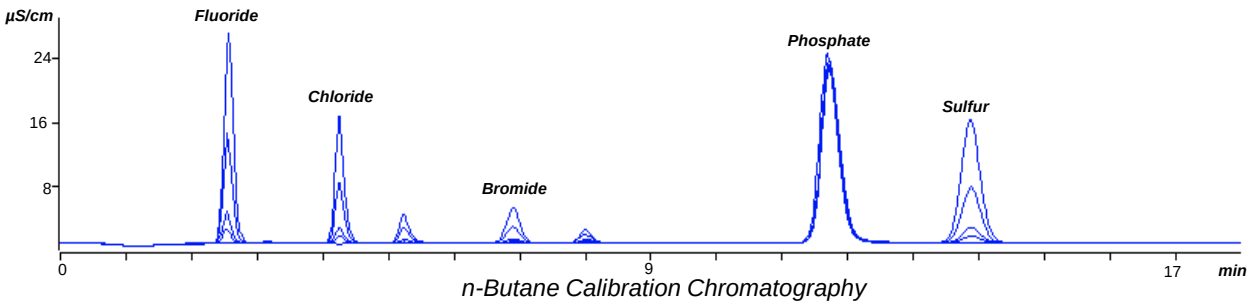
CONCLUSION

The results demonstrate that the MultiTek Analyzer coupled with Ion Chromatography provides a sensitive, automated and reliable analysis of halides and sulfur in liquefied petroleum gas. This analysis will allow the refinery and other processes to monitor concentration levels to improve plant safety and efficiency.



n-Butane Calibration Chromatography

Anteks MultiTek® is the only instrument on the market that combines testing sulfur, nitrogen, and halides all in one. Compact, powerful, automated, and multi-configurable, it's the perfect solution to today's increasing demand worldwide for fast, accurate detection and the analysis 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.

00.00.177 2012/1 - © Copyright 2012 PAC L.P. All rights reserved

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