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

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Introduction

Hydrofluoric acid alkylation is a 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 ($F/Cl/Br/SO_x$) 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 an atmosphere of steam, halogen containing compounds are converted into an acid gas state. Sulfur containing compounds are oxidized to sulfur dioxide (SO_2) and sulfite (SO_3) and analyzed as a linear occurence as sulfite and sulfate on the IC (Ion Chromatograph). 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 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

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

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

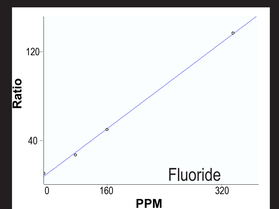
Instrumentation

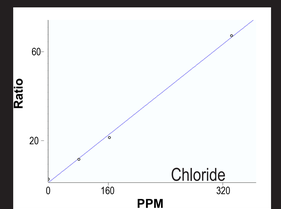
Antek MultiTek Horizontal, Antek Model 740 boat inlet system, Antek Model 735 syringe drive, Antek Model 734 Gas/LPG Sampler and suppressed IC system.

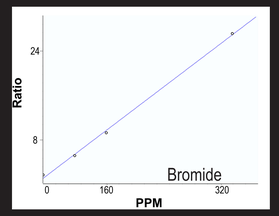
Instrument Parameters:

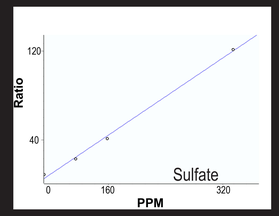
734 Sample Loop (µl)	15
IC Sample Loop (µl)	250
GFC1- Ar/He (ml/min)	130
GFC2- Pyro (ml/min) O_2	450
GFC4- Carrier (ml/min) O_2	30
GFC4- Carrier (ml/min) O_2	20
734 Carrier- Ar or He (ml/min)	20
Furnace (ºC)	1050
Sample Burn Time (mm:ss)	02:45

Calibration









Correlation and Standards

Correlation

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

0-300 ppm	Flouride	Chloride	Bromide	Sulfate
Correlation Coefficients	0.999	0.999	0.999	0.998
Curve Fit	Linear	Linear	Linear	Linear

Standards

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

Results

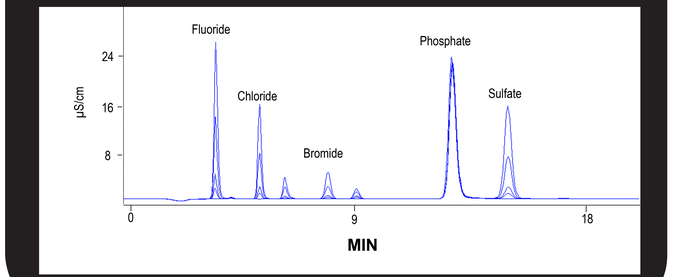
Repeatability of ~25 ppm (w/w) n-butane (n=6)

	Fluoride	Chloride	Bromide	Sulfate
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	Sulfate
LOD	374 ppb	164 ppb	46 ppb	1 ppm

N-butane Calibration Chromatography



Conclusion

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

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