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APPLICATION NOTE 42222

Elemental Analysis: Total oxygen determination in gasoline

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Goal

This application reports data of oxygen determination in gasoline samples, according to the ASTM D 5622-95 Method.

Introduction

Oxygenated compounds are added to unleaded gasoline as antioxidants and octane enhancers. The accurate determination of the amount of these compounds has become critical for quality control tests and for the compliance with current legislations.

According to ASTM D 5622-95 Method, total oxygen determination in gasoline and methanol fuels can be performed using reductive pyrolysis. The Thermo Scientific™ Flash*Smart*™ Elemental Analyzer equipped with the Thermo Scientific™ AS 1310 Liquid Autosampler (Figure 1) enables to perform elemental analysis by combustion and oxygen determination via pyrolysis. The Flash*Smart* Elemental Analyzer fullfills the requirements of accuracy and reproducibility and the standards required by ASTM D 5622-95 Method.

Methods

Gasoline samples are injected with a syringe into the pyrolysis reactor, at a temperature of 1060 °C. The reactor is set up with nickel coated carbon. The oxygen in the sample combined with the carbon forms CO, which is chromatographically separated from other gases and detected by a Thermal Conductivity Detector (TCD) (Figure 2). Total Run Time is 5 minutes.

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Figure 1. Flash*Smart* Elemental Analyzer with the AS 1310 Liquid Autosampler.

The thermoregulated Electronic Carrier Gas Flow Control (EFCt) ensures the stability of the analytical conditions, guaranteeing the reliability of the system throughout a sequence, and eliminating the need for frequent calibrations.

The Thermo Scientific™ AS 1310 Liquid Autosampler provides automated and unattended injection of the liquid samples up to 105 vials.

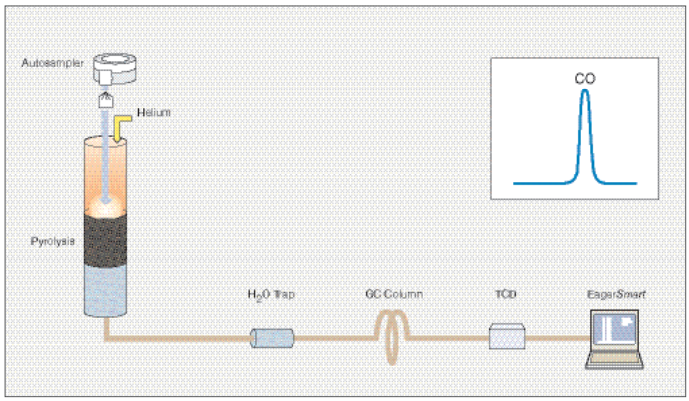

Figure 2. Oxygen configuration.

A report is generated by the Thermo Scientific™ Eager*Smart* Data Handling Software and it is displayed at the end of the analysis. With the Eager*Smart* Data Handling Software and the Liquid Autosampler are fully automated. Automated functions (Auto-Standby, Auto-Ready, Auto-Start) enable cost savings and higher laboratory throughput.

Analytical conditions	
Furnace Temperature:	1060 °C
Oven Temperature:	65 °C
Helium Carrier Flow:	100 mL/min
Helium Reference Flow:	100 mL/min
Standard:	Solution n-hexane/ethanol
Sample Volume Injected:	2–3 uL

ASTM D 5622-95 Method Requirements

1. Calibration: measure the response of the blank until stable value. Analyze two times the standard NIST SRM 1837 (6.57% O).
2. Quality control: analyze twice the standard NIST SRM 1838 (3.95% O), the results obtained must be within 2% relative with the certified value.
3. Repeatability: the difference between two consecutive test results must not exceed 0.06 for samples with 1.0 to 5% O.

Results

Applicability of the method was proven with solutions containing mixed quantities of n-hexane and ethanol. Table 1 shows the results and examples of the excellent reproducibility of the method, using either the AS 1310 Liquid Autosampler or manual injection.

Table 2 shows results of the NIST SRM 1837, used for calibration, and of the NIST SRM 1838, used for quality control. The SRM 1837 was analyzed twice at different times. The data of peak areas proved the stability of the system and the reproducibility of the injections. The results of the SRM 1838 met the certified value within 2% RSD.

Table 3 shows the results of a series of gasoline samples during different runs. Each sample was analyzed twice. The repeatability of the data exceeds the needed requirements of the ASTM method (less than 0.06).

Conclusions

For the the analysis of oxygen in gasoline according to ASTM D 5622-95 Method, the Thermo Scientific Flash*Smart* EA provides accurate data, which fulfill official method requirements. Thanks to its software controlled automated functions analyses are fast and overall operational costs are reduced.

Results of different analysis series show excellent reproducibility and meet the requirements of the ASTM D 5622-95 Method. No matrix effect was observed when changing the sample, meaning the total conversion of oxygen during the analysis.

Table 1. Oxygen analysis of a solution of n-hexane/ethanol (4.5 O%).

Injection Mode	AS 1310 Autosampler	Manual Injection
Oxygen %	4.4902	4.5184
	4.4962	4.4436
	4.5290	4.5320
	4.4721	4.5802
	4.5387	4.4841
	4.5172	4.4840
	4.4895	4.5303
	4.5371	4.4854
	4.5200	4.5642
	4.5132	4.4828
	4.4774	4.4832
	4.5346	4.4886
	4.5366	4.5421
	4.5029	4.5132
	4.4985	4.5402
Mean Oxygen %	4.5102	4.5115
Std. Dev.	0.0226	0.0367
RSD %	0.5019	0.8150

Table 2. Calibration response of SRM 1837 and accuracy of SRM 1838.

Sample	Data	Test 1		Test 2		Test 3		Test 4	
		Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
NIST SRM 1837 (6.57 O)	Area mv/sec	390510	380352	388289	379413	389888	379269	385273	384467
NIST SRM 1838 (3.95 O%)	Oxygen %	3.94	3.91	3.91	3.88	3.91	3.87	3.98	3.94
	Av.%	3.92		3.89		3.89		3.96	
	Difference from certified value	0.03		0.06		0.06		0.01	

Table 3. Repeatability of oxygen analysis in gasoline.

Sample	Test A		Test B		Test C	
	O%	RSD%	O%	RSD%	O%	RSD%
1	2.723–2.713	0.275	2.742–2.741	0.013	2.763–2.766	0.072
2	3.522–3.531	0.178	3.547–3.546	0.042	3.543–3.537	0.124
3	4.781–4.813	0.517	4.861–4.831	0.443	4.999–4.954	0.642
4	3.084–3.090	0.141	3.076–3.069	0.146	3.052–3.077	0.573
5	2.027–2.012	0.519	2.027–2.008	0.672	2.016–2.021	0.166
6	2.654–2.645	0.225	2.640–2.632	0.212	2.625–2.620	0.113

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