Application Note 10351

Analysis of Flue Gases with GC and TCD Detection

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Introduction

Flue gas is the gas that exits via a flue, which is a pipe or channel for conveying exhaust gases from a fireplace, oven, furnace, boiler, or steam generator to the atmosphere. Quite often, flue gas refers to the combustion exhaust gas produced at power plants. Its composition depends on what is being burned, but usually consists of mostly nitrogen (typically more than two-thirds) derived from the combustion air, carbon dioxide (CO_2), and water vapor as well as excess oxygen (also derived from the combustion air). It further contains a small percentage of a number of pollutants, such as particulate matter (like soot), carbon monoxide, nitrogen oxides, and sulfur oxides [1].Pulverized coal is usually used to fire the boiler of power plants. Due to safety reasons, monitoring of carbon monoxide (CO) in coal bunkers and coal mills is extremely important. CO is an odorless and very toxic gas and imposes a serious explosion threat at levels above 8 % vol.in air. Higher CO concentrations may indicate a seat of smouldering and require immediate counter measures. Moreover, oxygen concentrations provide significant information for coal grinding plants that are operated under inert purging conditions. An increasing oxygen concentration value indicates the entrance of false air into the system and thus protects against the risk of explosion. Flue gas analysis indicates the air-fuel ratio. Analysis of flue gases gives evidence of efficiency of combustion and is a prime factor in controlling the operation for maximum results [2]. In fact, the object of a flue gas analysis is to determine whether the carbon in the fuel has completely combusted and the amount and distribution of the heat losses due to incomplete combustion. In view of maintaining safety and productivity, monitoring of these gases, especially CO, CO_2, O_2, and CH_4 in flue gas are very important.

The quantities actually determined by an analysis are the relative proportions by volume of carbon dioxide (CO_2), oxygen (O_2), methane (CH_4), and carbon monoxide (CO). This can be achieved by using the Thermo Scientific™ TRACE™ 1110 GC equipped with a thermal conductivity detector (TCD) and valve oven as described below.

Experimental

Sample preparation

Calibration gas mixture consisted of the components from the flue gases, CO, CO_2, CH_4, O_2 and balance nitrogen. One mL of this calibration gas mixture was analyzed by the GC system.

GC Configuration

The GC system consisted of two columns, Porapak™ Q and Molecular Sieve 5A with valve oven and TCD. A typical schematic diagram of the valve oven is given in Figure1. The GC analytical conditions are listed in Table 1.

Table 1. GC Parameters with TCD and valve oven

Oven	50 °C, 15.00 min isothermal
	Multi cycle 00/01
Oven Max. Temperature	300 °C
Cryo Temperature	Disable
Injectors	
Injector 2	Packed column injector
Set Temperature	100 °C
Carrier Gas	Hydrogen
Injector	through 10 port GSV
Pressure	2.20 bar
Column Flow	25 mL/min
Ref Carrier Flow	25 mL/min
Column 1	8 ft. x1/8 in. Porapak Q
Column 2	8 ft. x1/8 ft. MolecularSieve 5A
Injector 3	Valve Oven
Set Temp	60 °C
Detector Parameters	
Detector	TCD
Det. BaseTemperature	200 °C
Det. Cell Temperature	180 °C
TCD Voltage	9.0 V
TCD Current	110 mA

Time Event Table

Event	ON Time [min]	Off time [min]	Function
1	0.30	1.00	Valve # 1 Sampling (1 mL Loop)
2	3.50	15.00	Valve # 2 Vent of Porapak Q
3	2.32	3.52	Valve # 3 Bypass of Mol.Sieve
4	0.03	0.24	Sample purge ON for 20 s

Results and Discussion

Sample Analysis and Repeatability

A calibration gas reference standard mixture typically comprises of the flue gases CO, CO_2, CH_4, O_2 and balance nitrogen. One mL was injected into the TRACE 1110 GC system. The GC chromatogram is shown in Figure 2. CO_2 is analyzed on the Porapak Q column, while the other gases, O_2, N_2, CH_4 and CO, are being analyzed on the Molecular Sieve 5 A column. Repeatability studies were conducted, and the data is displayed in Table 2.

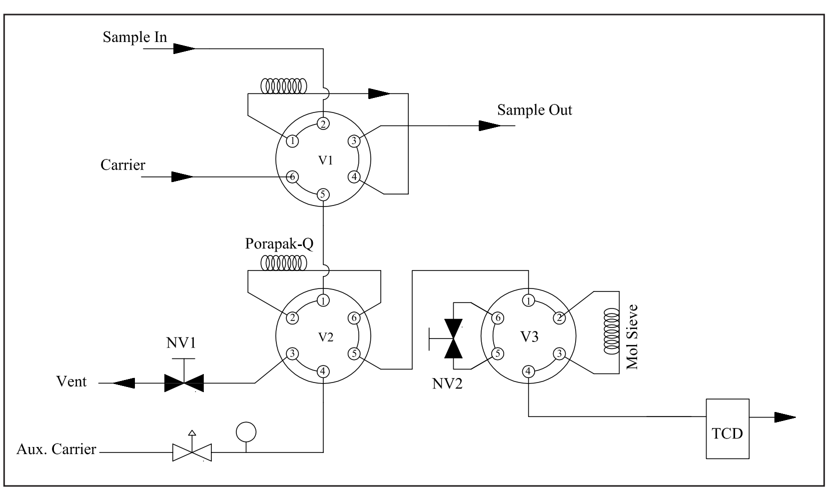
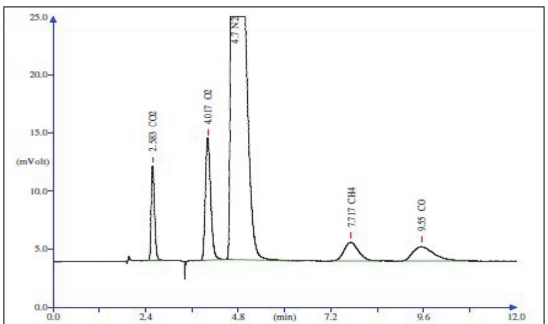


Figure1. TRACE 1100 GC Flue Gas Analyzer - Schematic diagram of the valve oven installation.

Table 2. Repeatability results of the reference gas standard mixture.

Area Repeatablity of Flue Gas Test Mixture Analysis on TRACE 1100 GC Analyzer with Valve Oven							
Group	Sample name	File name	CO_2	O_2	N_2	CH_4	CO
			[area cts]	[area cts]	[area cts]	[area cts]	[area cts]
2	Flue Gas Mix002	TKA_TCD002	828921	1224548	14643030	696541	810227
2	Flue Gas Mix003	TKA_TCD003	830019	1225539	14639834	694738	797767
2	Flue Gas Mix004	TKA_TCD004	830464	1224914	14643026	684647	798595
2	Flue Gas Mix005	TKA_TCD005	823019	1223752	14631452	689465	801357
2	Flue Gas Mix006	TKA_TCD006	822968	1226574	14629706	708777	812695
		Average	827078	1225065	14637410	694834	804128
		STDEV	3771	1063	6400	9082	6880
		% RSD	0.46%	0.09%	0.04%	1.31%	0.86%



Peak Number #	Area %	Ret.Time	Area	BC
CO2	3.4654	2.58	486798	RS
O2	7.1787	4.02	1008418	FU
N2	83.1005	4.70	11673360	FU
CH4	2.9593	7.72	415698	RS
CO	3.2961	9.55	463007	RS
Totals	100.0000		14047280	

Figure2. GC chromatogram of the flue gas components.

Conclusion

The TRACE 1110 GC can be configured for a routine flue gas analysis with the two specific separation columns Porapak Q and Molecular Sieve 5A using a valve switching system and thermal conductivity detector (TCD).

The complex composition of the flue gas with CO_2, CO, O_2, CH_4 and N_2 can be successfully analyzed with good compound separation and repeatability. An excellent precision with relative standard deviations significantly below 2 % can be achieved in routine applications.

References

1) Beychok, M., Fossil fuel combustion flue gases (2012). Retrieved from http://www.eoearth.org/view/article/171355.

2) Mitchell, A.A., Gas Appliance Engineer's Handbook, Section 3, Flue Gas Analysis, 1965.

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