

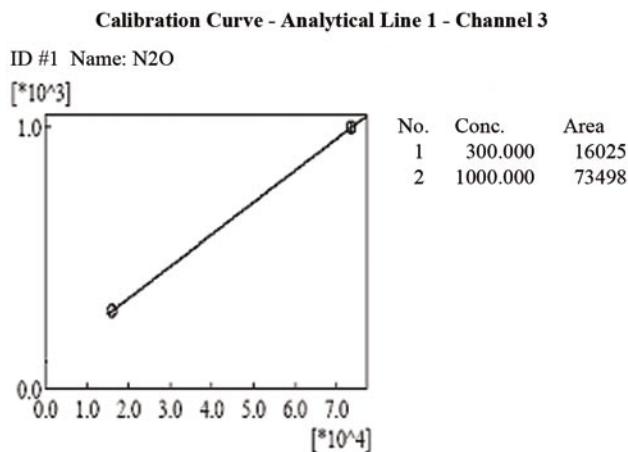
# GC Analysis of Greenhouse Gases and Optional Headspace Automatic Sample Introduction

Global warming and pollution have aroused interest in the monitoring and study of various atmospheric gases that absorb the sun's rays. These gases, CO<sub>2</sub>, Methane and Nitrous Oxide, are present in the atmosphere and, through a variety of means, are thought to be increasing in concentration. This document outlines the various means by which each of these gases may be measured using GC and a variety of detectors. Typical greenhouse gas samples are contained within a matrix of atmospheric air, requiring chromatographic separation. Often, samples contain water, which can interfere with the chromatographic separation or detection mechanism or damage a detector.

Shimadzu Scientific Instruments has designed a variety of GC systems for the quantitative analysis of greenhouse gases. The systems are described in this document.

## System 1

This system utilizes three detectors, four 1/16th inch valves and six columns. It is designed to analyze the three gases in a matrix of atmospheric air containing water vapor. Maximum sensitivity is achieved by simultaneously injecting 1 ml of sample using fixed loops. The Nitrous Oxide section of the system consists of two valves: a ten-port valve plumbed for loop injections and back-flush of pre-column to vent. Downstream of the ten-port valve is a four-port valve that is plumbed to heart cut oxygen and divert it away from the Electron Capture detector to a vent. Two columns are used for the separation of Nitrous Oxide from the air matrix. Water is back-flushed from the Haysesep T pre-column while providing primary separation of Nitrous Oxide from air. Nitrous Oxide is further separated from air on the second column.

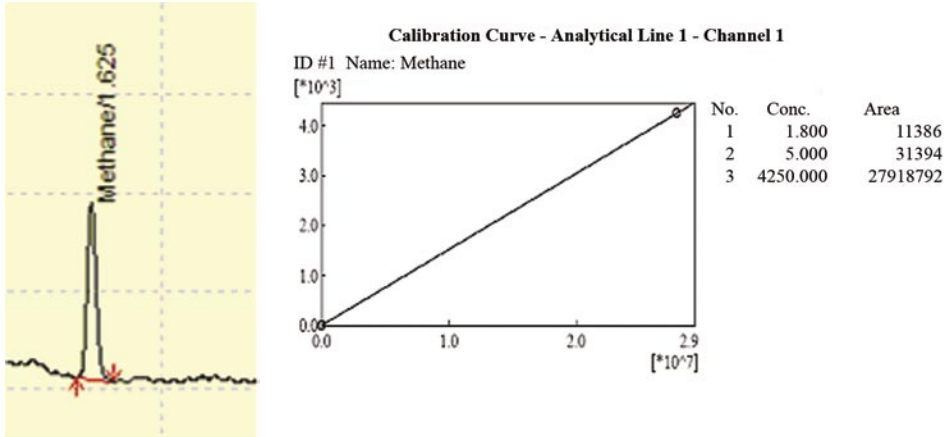


*N2O: 300ppb in air with Helium carrier with P5 make-up gas.*

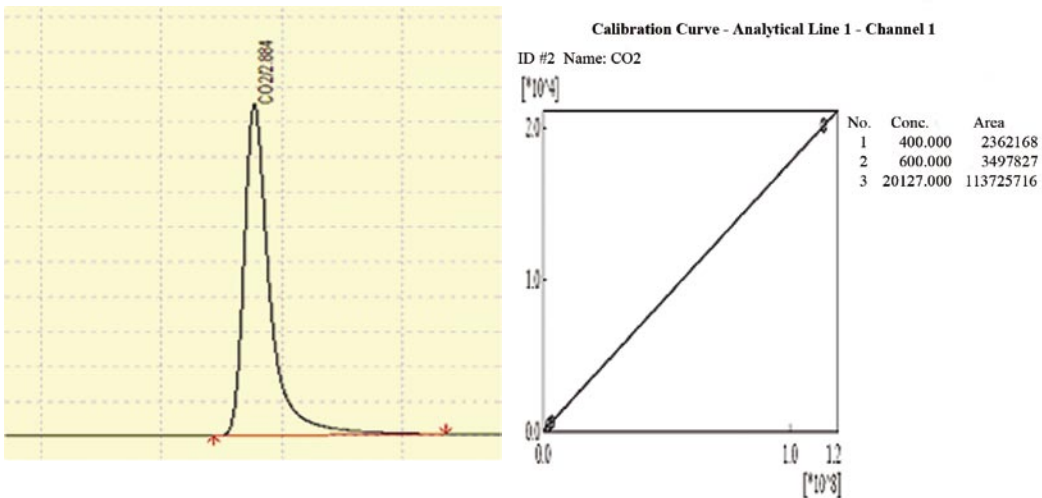


Methane and Carbon Dioxide are quantitatively analyzed using two valves: a ten-port valve for loop injections and pre-column back-flush to vent, then a six-port column switching valve. The sample is injected on to the Haysesep T pre-column where the air, CO<sub>2</sub> and CH<sub>4</sub> are separated from water. Water is back-flushed out of the system while air is further separated into O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub>. A TCD is used for the detection of O<sub>2</sub>, N<sub>2</sub> and CO<sub>2</sub> and is tied in series to a methanizer and FID. Detection of low levels are obtained for CO<sub>2</sub> by conversion to CH<sub>4</sub> and detection by FID. Oxygen, Nitrogen and Carbon Monoxide are also separated and can be analyzed with this system.

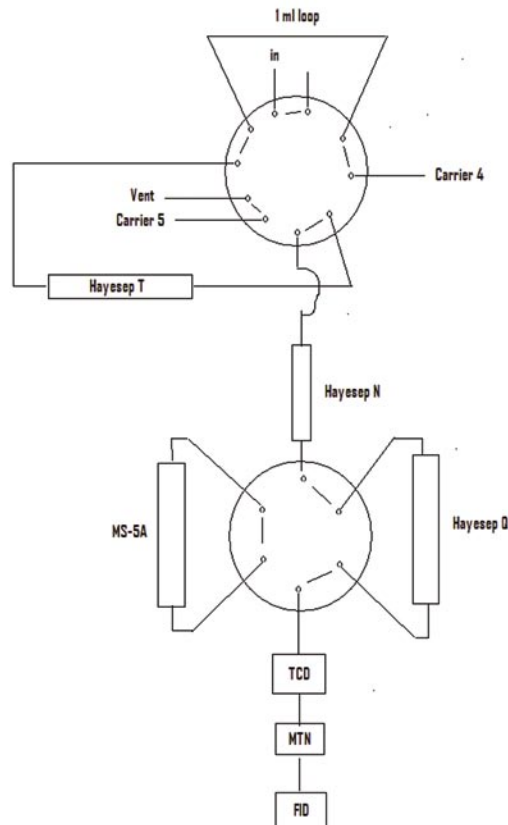
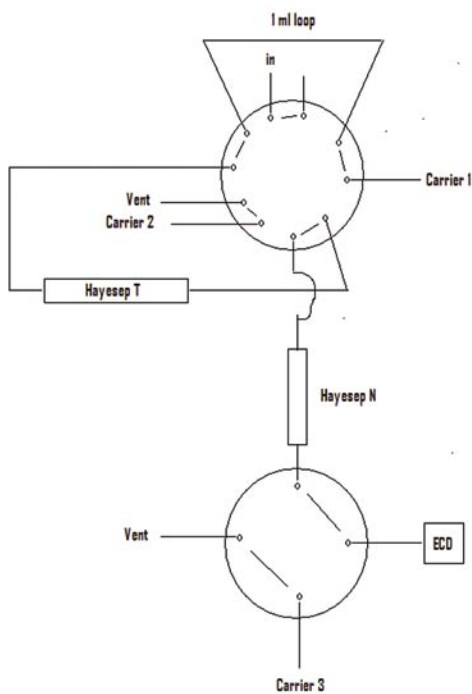
#### 1.8ppm (approximate) Methane by FID



#### 400ppm (approximate) CO<sub>2</sub> by Methanizer and FID



## Plumbing Diagram of System 1



### Hardware

- GC-2014, TCD, FID, ECD
- 2 Ten-Port 1/16 inch Valves
- 1 Four-Port 1/16 inch Valve
- 1 Six-Port 1/16 inch Valve
- Injection Port Methanizer with Nickel catalyst

### Required Gases

- Hydrogen
- Air
- Helium
- P5 (5% Methane in Argon)

### Detection and Quantitation Limits

- N<sub>2</sub>O: 50ppb to 100ppm by ECD
- CO<sub>2</sub>, CO: 10ppm to 10% by TCD and 1ppm to 1% by Methanizer and FID
- CH<sub>4</sub>: 0.1ppm to 1% by FID
- N<sub>2</sub>, O<sub>2</sub>: 100ppm to 20% by TCD

**For System #1, please reference part #220-94725-00.**

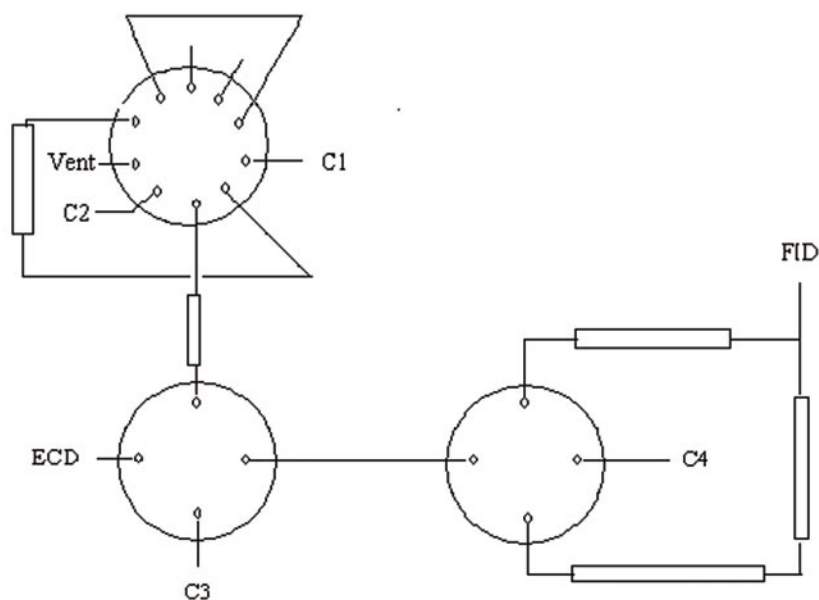
*Detection limits are based on a 1 ml injection volume of atmospheric air containing 0 to 80% relative humidity.*



## System 2

This system utilizes three valves and two detectors. The Nitrous Oxide section is identical to System 1 as described. The Carbon Dioxide and Methane are diverted to another four-port valve where they are directed to parallel columns. The Methane is sent directly to the FID, and the Carbon Dioxide is sent to a methanizer before detection by FID. This system is less expensive due by eliminating the fixed-gas separation. Detection limits are the same for both systems.

### Plumbing Diagram of System 2



#### Hardware

- GC-2014, FID, ECD
- 1 Ten-Port 1/16 inch Valve
- 2 Four-Port 1/16 inch Valves

#### Required Gases

- Hydrogen
- Air
- Helium
- P5 (5% Methane in Argon)

#### Detection Limits

- N<sub>2</sub>O: 50ppb to 100ppm by ECD
- CO<sub>2</sub>: 1ppm to 1% by FID
- CH<sub>4</sub>: 0.1ppm to 1% by FID

*For System #2, please reference part #220-90804-24.*

*Detection limits are based on a 1 ml injection volume of atmospheric air containing 0 to 80% relative humidity.*

### Automatic Sample Introduction

Analyses of either system can be accomplished with the addition of the CTC AOC-5000 static headspace autosampler. Precision of 3 to 5 % RSD for the various gases is achieved; however, it is not recommended for System #1 if O<sub>2</sub> and N<sub>2</sub> are to be quantified.

*For the AOC-5000, please reference part #220-90778-01. For the mount kit for the GC-2014, please reference part #220-94500-43. For Cycle Composer Software, please reference part #220-91180-33.*

