GC Analysis of Greenhouse Gasses

Global warming and pollution have aroused interest in the monitoring and study of various atmospheric gasses that absorb the sun’s rays. These gasses, CO2, 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 gasses 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, detection mechanism or damage a detector.

Shimadzu Scientific Instruments has designed a variety of GC systems for the quantitative analysis of Greenhouse gasses. 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 gasses 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. Down stream of the ten-port valve is a four-port valve, which 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 precolumn while providing primary separation of Nitrous Oxide from air. Nitrous Oxide is further separated from air on the second column.

![N2O: 100ppb in air with Helium carrier with P5 make-up gas](image-url)
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 Haysep T pre-column where the air, CO2 and CH4 are separated from water. Water is back-flushed out of the system while air is further separated into O2, N2, CH4 and CO2. A TCD is used for the detection of O2, N2 and CO2 and is tied in series to a methanizer and FID. Detection of low levels are obtained for CO2 by conversion to CH4 and detection by FID. Oxygen, Nitrogen and Carbon Monoxide are also separated and can be analyzed with this system.

**400 ppm (approximate) CO2 by Methanizer and FID**

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

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

**Detection and Quantitation Limits**
- N2O: 50ppb to 100ppm by ECD
- CO2: 10ppm to 10% by TCD and 1ppm to 1% by Methanizer and FID
- CH4: 0.1ppm to 1% by FID

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 three detectors. The Nitrous Oxide section is identical to System 1 as described previously. The Carbon Dioxide and FID section utilizes a ten-port valve, Flame Ionization and Thermal Conductivity detectors. No methanizer or fixed-gas separation is performed. Advantages are:

1) Increased ruggedness by eliminating the methanizer  
2) Less expensive by eliminating the fixed gas separation

Detection limit of Carbon Dioxide will be higher but still adequate for atmospheric samples.

**Plumbing Diagram of System 2**

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

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

**Required Gasses**  
• Hydrogen  
• Air  
• Helium  
• P5 (5% Methane in Argon)

**Detection and Quantitation Limits**  
• N2O: 50ppb to 100ppm by ECD  
• CO2: 10ppm to 10% by TCD  
• CH4: 0.1ppm to 1% by FID