Simultaneous Analysis of Greenhouse Gases by Gas Chromatography

Application

Environmental

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Abstract

Two analytical methods based on the Agilent 7890A GC system are developed for simultaneous analysis of methane (CH_4), carbon dioxide (CO_2), nitrous oxide (N_2O) in air samples. Each system has its own features to meet different requirements of greenhouse gases analyses. Both systems can easily be expanded to determine sulfur hexafluoride (SF_6). Results from both methods demonstrated high sensitivity and excellent repeatability for the required analyses.

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Introduction

Carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) are considered the main greenhouse gases in the Earth's atmosphere. These gases trap heat in the atmosphere and affect the temperature of the Earth. Continuous measurement of these gases provides meaningful information to track greenhouse gas emission trends and help in the fight against climate change. On January 1, 2010, the U.S. Environmental Protection Agency will require large emitters of heat-trapping emissions to begin collecting greenhouse gas data under a new reporting system [1].

Two different configurations of Agilent 7890A GC systems have been developed for greenhouse gas analysis. These systems can also be used for other samples such as soil gases analysis or plant breathing studies where the analytes of interest contain gases such as CH_4, N_2O and CO_2 [2].

Method 1: SP1 7890-0468

An Agilent 7890A GC system is configured with a single channel using two detectors (FID and micro-ECD) for the analysis of CO_2, CH_4, N_2O, and SF_6 in air samples. Low concentrations of CO_2 can be analyzed by a methanizer with an FID.

Method 2: SP1 7890-0467

An Agilent 7890A GC is configured with two separate channels using three detectors (FID, TCD and micro-ECD) for the analysis of CO_2, CH_4, N_2O, and SF_6 in air samples. CO_2 can be analyzed at wide concentration levels. High levels of CO_2 can be analyzed by TCD and low concentrations can be analyzed by a methanizer with an FID.

A dynamic blending system is used to prepare the low level calibration standards using N_2 as a diluent.

Experimental and Results

Method 1: SP1 7890-0468

This system has three valves and two detectors using 1/8-in stainless steel packed columns (HayeSep Q 80/100). The methanizer/FID combination is used to measure low levels of CH_4 and CO_2, while the micro-ECD detects N_2O. The valve diagram is shown in Figure 1. The system can be modified to use a 6-port valve instead of a 10-port for automated headspace sampling. The typical GC conditions for Method 1 are listed in Table 1.

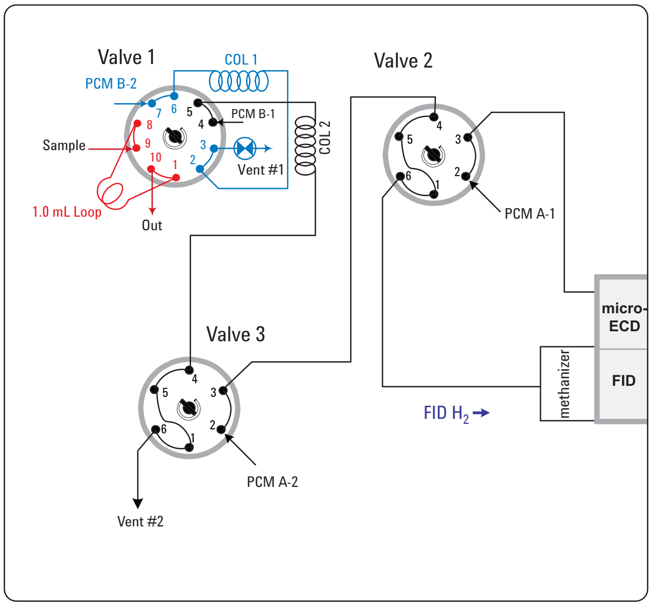

Figure 1. Configuration for SP1 7890-0468.

Table 1. Typical GC Conditions for Greenhouse Gas Analysis using Method 1

7890A GC	
Valve temperature:	100 °C
Oven temperature:	60 °C
Post run at oven temperature of 110 °C for 2 minutes is recommended	
Methanizer Temperature:	375 °C
Sample loop:	1 mL
Column 1, 2 flow (N_2):	21 mL/min (at 60 °C), constant pressure
FID	
Temperature :	250 °C
H_2 flow:	48 mL/min
Air flow:	500 mL/min
Make-up (N_2):	2 mL/min
micro-ECD	
Temperature :	350 °C
Make-up, 5% methane in Argon (Ar/5%CH_4):	2 mL/min
Concentration of Gas Sample Standards	
CH_4:	20.18 ppm v
CO_2:	376.4 ppm v
N_2O:	3.27 ppm v

Figure 2 illustrates a chromatogram of gas sample standards using Method 1. The sample is injected into a short HayeSep Q (column 1) which separates the components including air, CO2 and CH4 from water. All analytes after N2O are back-flushed to vent 1. Air (O2) should be directed away from the methanizer and micro-ECD and vented through vent 2. CO2 is converted to CH4 through the methanizer and measured by FID as shown in Figure 2B. After CO2 elutes from column 2, the effluent is introduced to micro-ECD for measuring N2O as shown in Figure 2A.

A repeatability study with 21 consecutive analyses was performed with results tabulated in Table 2. Excellent peak area repeatability for the analysis of CH_4, CO_2, and N_2O standards was observed with this configuration.

Table 2. Repeatability for Greenhouse Gas Standards (n=21, Excluding the First Run)

Name	Average (Area)	STDVE	RSD%
CH_4	149.26	0.29	0.20
CO_2	2779.04	17.16	0.62
N_2O	8253.96	11.06	0.13

To improve the sensitivity of micro-ECD, Ar-5% CH_4 is recommended as the make-up gas, which can lower the detection of N_2O to approximately 32 ppb with the good signal-to-noise (S/N) ratio as shown in Figure 3. The injected standard is prepared by dynamic blending with a 100-times dilution.

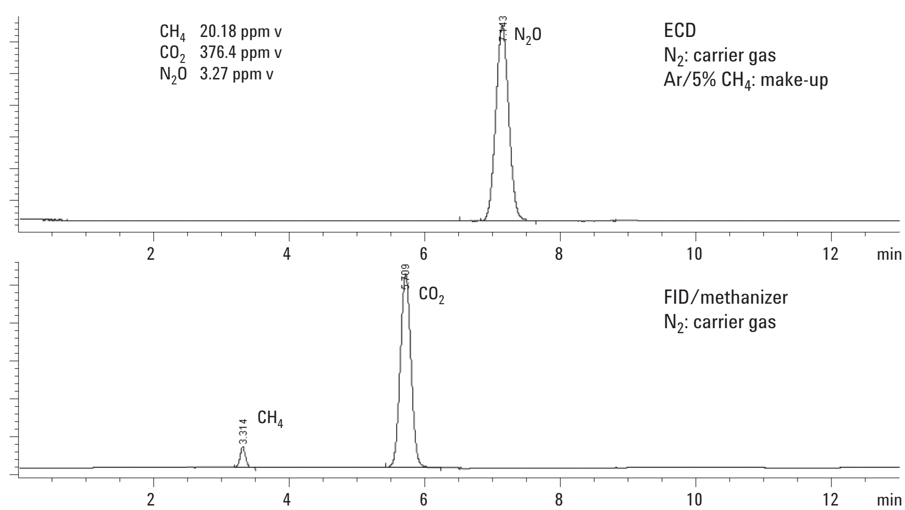

Figure 2. Analysis of greenhouse gases standards using Method 1.

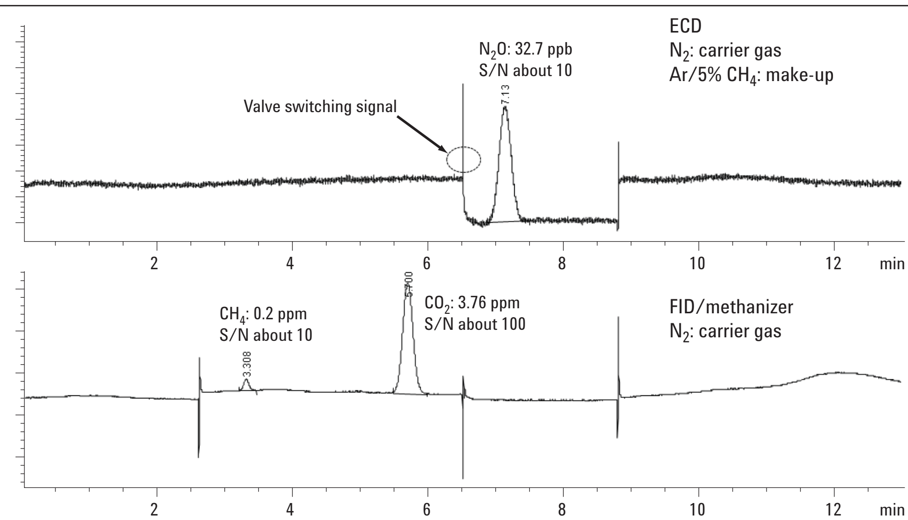

Figure 3. Chromatogram using Method 1 for CH_4, CO_2, and N_2O standards with a 100-times dilution.

The same configured system was used to analyze real samples. In this experiment, laboratory air is analyzed with Method 1. The chromatogram is shown in Figure 4. The measured concentrations of N_2O, CH_4, and CO_2 are 473 ppb, 2.7 ppm, and 380 ppm respectively.

The system can easily include the analysis of SF_6 by delaying the backflush time (valve 1) to allow SF_6 to elute into column 1 (precolumn). Figure 5 shows the chromatogram of SF_6 at approximately 0.5 ppb with a 1-mL sample size. The 0.5 ppb SF_6 standard is prepared by dynamic blending with 200 times dilution of the standard (original standard of SF_6 is 100 ppb).

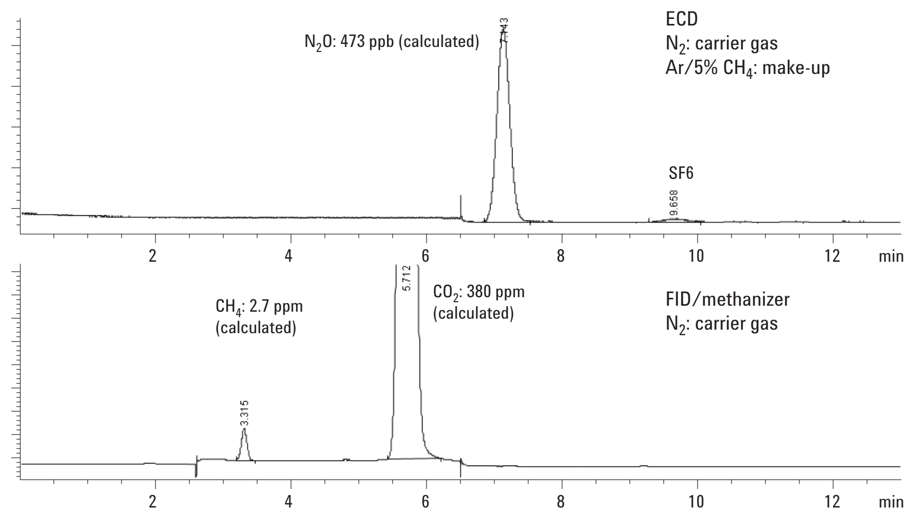

Figure 4. Chromatogram of real sample (laboratory air).

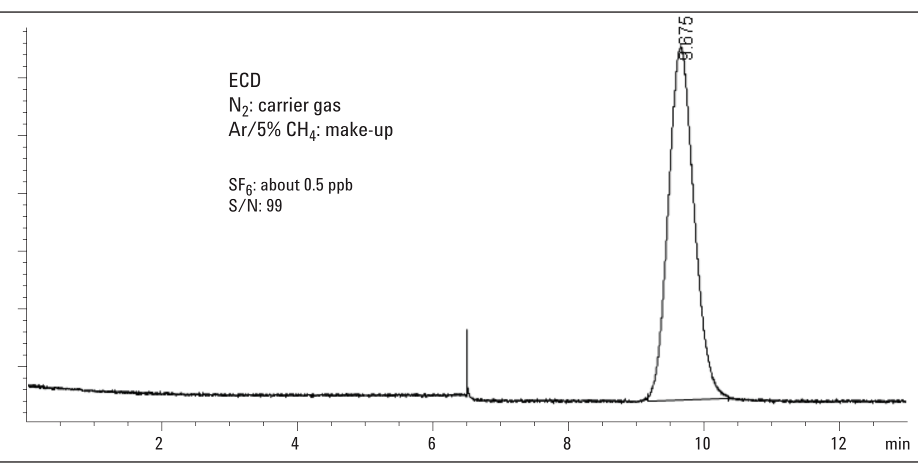

Figure 5. Chromatogram of SF_6 standard at approximately 0.5 ppb.

Method 2: SP1 7890-0467

This system consists of two separate channels with 1/8-in stainless steel packed columns (HayeSep Q 80/100). The first channel employs two valves with TCD and FID. The TCD and methanizer-FID are connected in series to measure CH_4 and CO_2. This channel provides the flexibility for CO_2 in varying levels. Low level CO_2 can be converted to CH_4 through the methanizer and measured by FID. The system is flexible depending on the requirements. The TCD can be used for high concentrations of CO_2. If only higher levels of CO_2 (higher than 50 ppm) analysis is required, the methanizer can be removed. This channel can be expanded to include O_2 and N_2 analysis by adding an additional Molsive column.

Another micro-ECD channel with two valves is dedicated to measuring N_2O and SF_6. Precolumns (column 1 and 2) direct heavier components (mainly water) to be backflushed to vent 1 and vent 4. O_2 should be excluded from the methanizer and micro-ECD and vented through vent 2 and vent 3. A typical plumbing diagram for this setup is shown in Figure 6. Typical GC conditions for Method 2 are listed in Table 3.

Table 3. Typical GC conditions for Greenhouse Gas Analysis Using Method 2

Valve temperature:	100 °C
Oven temperature:	60 °C
Post run at oven temperature of 110 °C for 2 min is recommended	
Sample loop:	1 mL
Column 1, 2 flow (He):	21 mL/min (at 60 °C), constant pressure
Column 3, 4 flow (N_2):	21 mL/min (at 60 °C), constant pressure
FID	
Temperature:	250 °C
H_2 flow:	48 mL/min
Air flow:	500 mL/min
Make-up (N_2):	2 mL/min
TCD	
Temperature:	200 °C
Reference flow:	40 mL/min
Make-up:	2 mL/min
micro-ECD	
Temperature:	350 °C
Make-up, Ar/5% CH_4:	2 mL/min
Methanizer Temperature :	375 °C

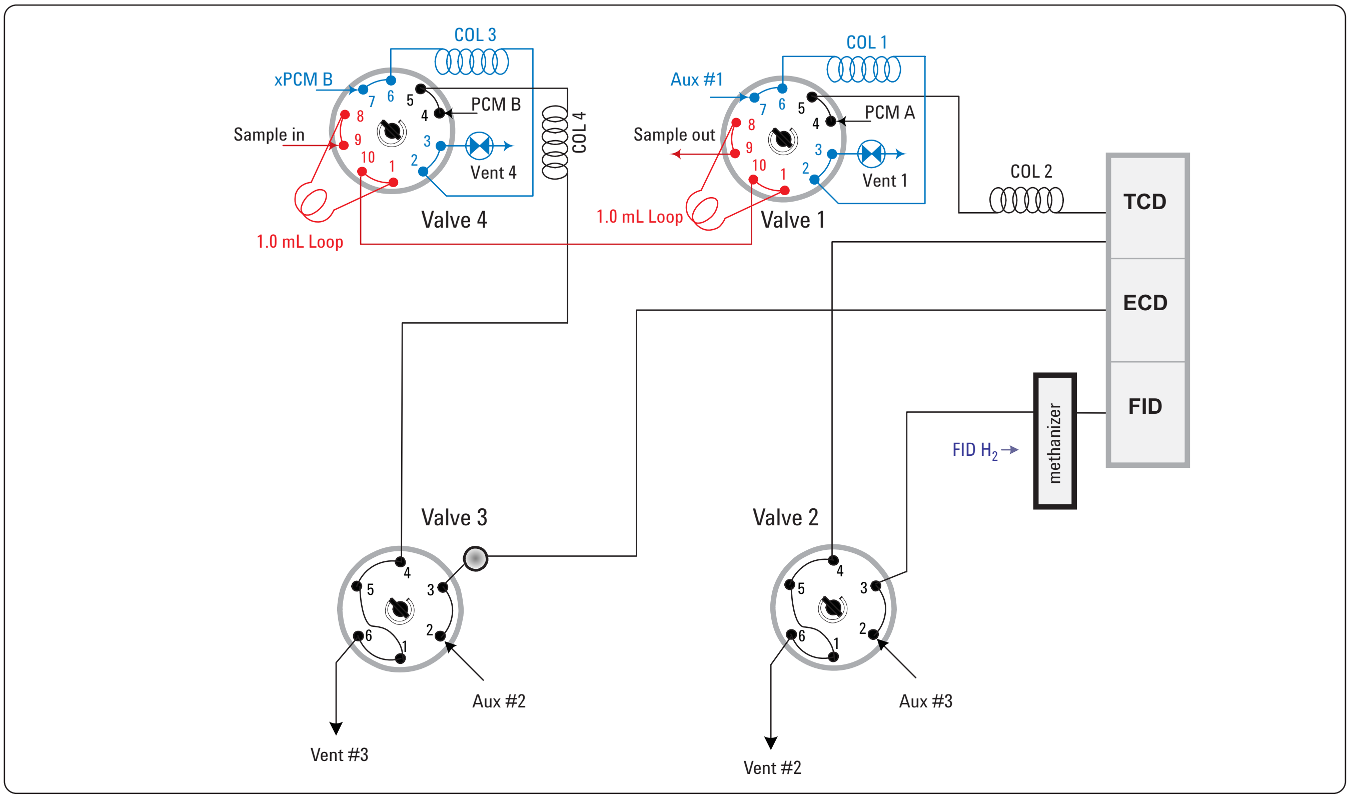

Figure 6. Valve configuration for Method 2.

Results obtained for greenhouse gases (N_2O, CH_4, CO_2 and SF_6) by Method 2 are equivalent to those obtained by Method 1. In addition, with this setup, high levels of CO_2 can now be measured by the third detector, TCD. The dynamic blending system is also used for Method 2 to prepare the low level standards. Table 4 shows very good repeatability of peak areas for the analysis of the greenhouse gas standards.

Table 4. Repeatability for Greenhouse Gas Standards (n=20, Excluding the First Run)

Name	Average (Area)	STDVE	RSD%
CH_4	151.61	0.64	0.42
CO_2(FID)	2788.51	14.72	0.53
N_2O	7467.92	13.91	0.19
CO_2(TCD)	186.00	0.80	0.43

Real sample (laboratory air) is analyzed with Method 2. The chromatogram is shown in Figure 7. The concentrations of N_2O, CH_4 and CO_2 measured are 441 ppb, 2.2 ppm and 398 ppm respectively.

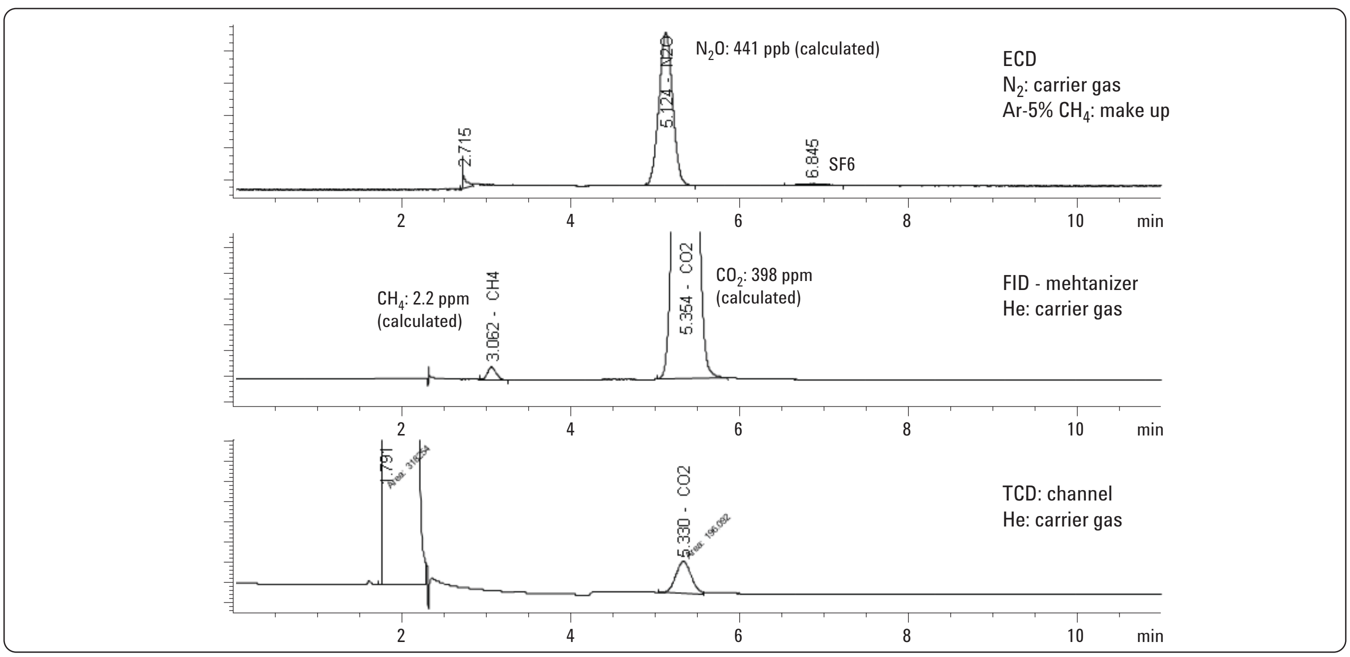

Figure 7. Chromatogram for real sample (laboratory air) using Method 2.

Conclusion

Two Agilent 7890A GC systems have been developed to meet the different requirements for simultaneous analyses of greenhouse gases including CH_4, CO_2, and N_2O in air samples.

Method 1 (SP1 7890-0468) has a simpler valve configuration and with minor modifications, accomodates autosampling by a headspace sampler.

Method 2 (SP1 7890-0467) has two separate channels with three detectors and can achieve even faster results. The separate channels increase flexibility to make the valve switching time less critical and the method easier to set up. The use of the third TCD allows measurement of a wide concentration range of CO_2 (0.2 ppm to 20%).

Results obtained on both analyzers are the same for greenhouse gases (N_2O, CH_4, CO_2 and SF_6).

References

1. Environmental Protection Agency (EPA), "40 CFR Parts 86, 87, 89 et al. Mandatory Reporting of Greenhouse Gases; Final Rule".
2. Teri Kanerva, Kristiina Regina, Kaisa Ramo, Katinka Ojanpera, Sirkku Manninen, "Fluxes of N_2O, CH_4 and CO_2 in a meadow ecosystem exposed to elevated ozone and carbon dioxide for three years", Environmental Pollution 145 (2007) 818-828.
3. European Environment Agency, Manual for the EEA greenhouse gases data viewer.

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