

## Quick Measurement of CH<sub>4</sub>, CO<sub>2</sub> and N<sub>2</sub>O Emissions from a Short-Plant Ecosystem

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### ABSTRACT

Combining improved injector, gas line and valve-driving models, a gas chromatograph (GC) equipped with Hydrogen Flame Ionization Detector (FID) and Electron Capture Detector (ECD), can measure CH<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub>O simultaneously in an air sample in four minutes. Test results show that the system has high sensitivity, resolution, and precision; the linear response range of the system meets the requirement of flux measurements in situ. The system is suitable for monitoring fluxes of the main greenhouse gases in a short-plant field since it is easy to use, efficacious, and constant and reliable in collecting data.

**Key words:** gas chromatograph, valve, emission of greenhouse gases, ecosystem

Measurements of CH<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub>O fluxes are important for characterizing the source and sink of greenhouse gases (GHGs) and mitigating the emissions. Several methods are available for measuring these gases: (1) the eddy covariance technique, (2) dynamic-chamber techniques, (3) static-chamber techniques (Baldocchi et al., 1996; Swinbank, 1951; Norman et al., 1997). However, each method has different advantages, disadvantages, and susceptibility to measurement errors. The eddy covariance technique causes nearly no disturbance on the earth's surface, but requires adequate fetch and specialized instruments that are expensive and difficult to maintain (Swinbank, 1951). The dynamic-chamber method is also difficult to apply because of critical conditions and expensive instruments. The static-chamber method is widely applicable and characterized by a simple principle, cheap instrument, easy operation and multi-site observations (Norman et al., ; Wang, 1999). With the development of gas chromatography (GC), a static-chamber/GC system becomes more convenient for the measurement of GHGs. But before our improvements of GC, a detector can only measure one kind compound once injected. Combining improved injector, gas line, and valve-driving models, a GC equipped with FID and ECD, can measure CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O in an air sample simultaneously in four minutes. It enhances the efficiency of GC and shortens the period of analysis, and is more suitable for quick measurement

of GHGs emissions from a short-plant ecosystem.

The gas line of a GC bought from a company (4890D GC, Agilent Co. Produced) should be improved to connect it to an auto-sampler so that the instrument can be applied to measure CH<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub>O emissions simultaneously. The auto-sampling assembled module, which has national patents (Patent Nos. ZL92100938.0 and ZL96249356.2), were developed by the first author in 1992 and 1996, respectively (Wang et al., 1994; Wang et al., 1997). The system's basic principle is that a computer program sends instructions to control electronic circuit, and gas flow direction and to receive signal; solenoid valves selected are "normally open" or "normally close" to introduce the direction of compressed air flow, so as to control the process of auto-sampling, analyzing, and back-flushing. The system consists of (1) the gas supply section, (2) auto-sampling section, and (3) analysis and detection section. Figure 1 shows schematic drawing of the system, and the GC parameters used in the field laboratory are listed in Table 1.

Stability is an important index that may imply the characteristics of the GC. CH<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub>O are measured by this system under the conditions shown in Table 1. Results show that the average responsible factor (RF) of CH<sub>4</sub> spanning 2.02–60.6 ppmv is 0.00032, and coefficient of variation (CV) is 0.11% to 0.25% (9 injections). RF of CO<sub>2</sub> spanning 356–4020

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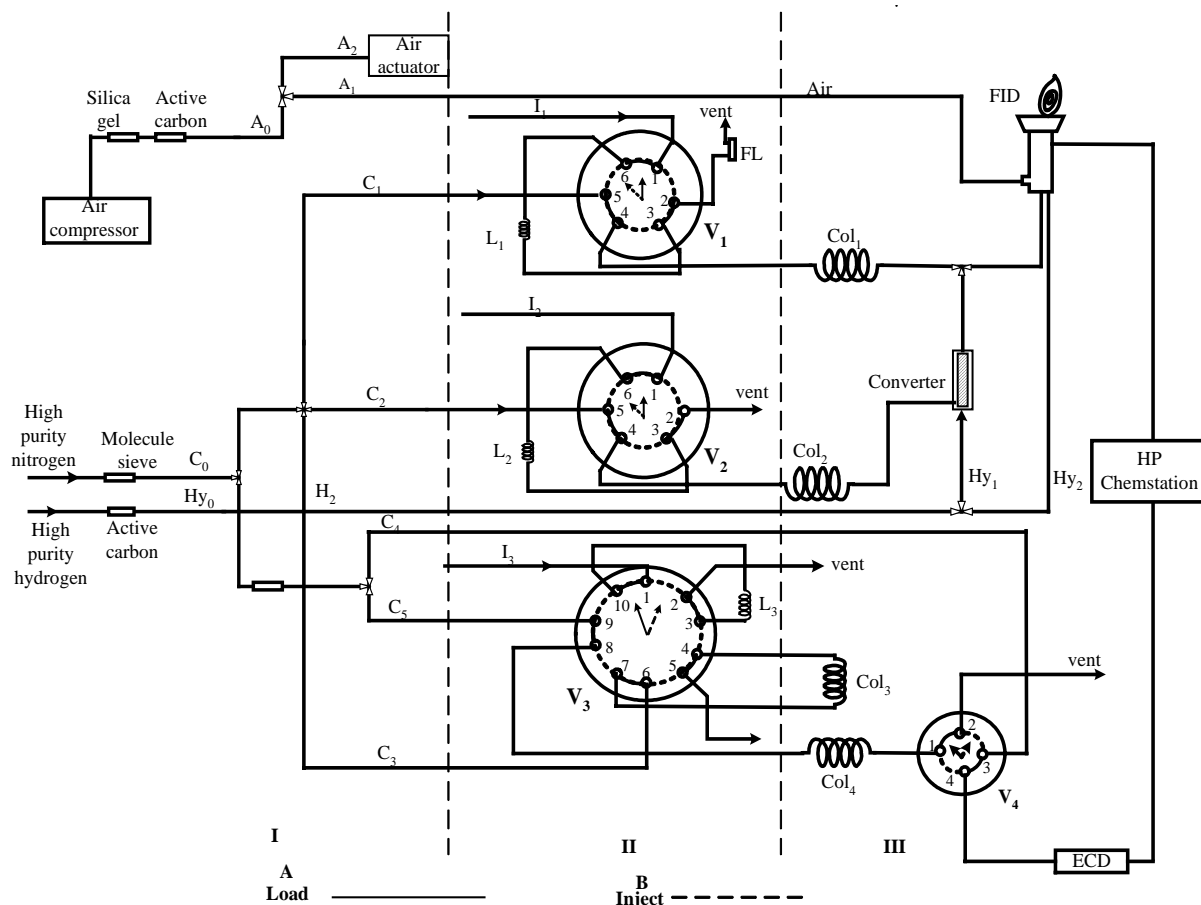


Fig. 1. Schematic drawing of  $\text{CH}_4$ ,  $\text{CO}_2$  and  $\text{N}_2\text{O}$  analysis gas pathway.

ppmv is 0.00047, and CV is 0.07% to 0.20%. RFs of  $\text{N}_2\text{O}$  in low concentration (333–2753 ppbv) and high concentration (3362–9412 ppbv) are 0.069 and 0.093, respectively, and CV in 3362–9412 ppbv is 0.31% to 0.48%. Obviously, CVs of  $\text{CH}_4$ ,  $\text{CO}_2$ , and  $\text{N}_2\text{O}$  are smaller than the level of 1% for the research project of “CBTSEC” measurement. The sensitivity and stability of the system completely satisfy the analysis of  $\text{CH}_4$ ,  $\text{CO}_2$ , and  $\text{N}_2\text{O}$  emissions from a short-plant ecosystem.

When  $\text{CH}_4$  and  $\text{CO}_2$  concentrations are in 2.02–60.6 ppmv and 356–4020 ppmv (normally, collected sample concentrations from a chamber in a terrestrial ecosystem will not exceed the upper limit), RFs of  $\text{CH}_4$  and  $\text{CO}_2$  are constant and their average CVs are 3.16% and 3.01%, respectively.  $\text{CH}_4$  and  $\text{CO}_2$  concentrations of air samples from a terrestrial ecosystem can be calculated by an external calibration curve. As for  $\text{N}_2\text{O}$ , different kinds of external calibration curves are used to calculate its emission flux in low or high concentration samples.

Analysis precisions of samples are:  $\text{CH}_4 \pm 32$  ppbv,

$\text{CO}_2 \pm 1.29$  ppmv and  $\text{N}_2\text{O} \pm 5.0$  ppbv, and concentrations of compound for those precisions are  $\text{CH}_4$  2.02 ppmv,  $\text{CO}_2$  524 ppmv, and  $\text{N}_2\text{O}$  333 ppbv. When atmosphere pressure is 1000 hPa, air temperature is 298 K, and chamber height is 50 cm or 100 cm (the two heights usually being employed in practice), exposure time is 10 minute. The flux detect abilities of  $\text{CH}_4$ ,  $\text{CO}_2$ , and  $\text{N}_2\text{O}$  are  $0.062 \text{ mg m}^{-2} \text{ h}^{-1}$  or  $0.124 \text{ mg m}^{-2} \text{ h}^{-1}$ ,  $6.89 \text{ mg m}^{-2} \text{ h}^{-1}$  or  $13.78 \text{ mg m}^{-2} \text{ h}^{-1}$ ,  $0.027 \text{ mg m}^{-2} \text{ h}^{-1}$  or  $0.053 \text{ mg m}^{-2} \text{ h}^{-1}$ , respectively.

Continuous measurement engaged in an ecological network for several years has demonstrated that this system can run steadily in the field and the maintenance of the system is convenient. The system is very important to study synthetically the effects of GHG emissions from a terrestrial ecosystem, and it is a reliable means to monitor net carbon flux and accomplish the great project of the knowledge innovation program of “Study on Carbon Budget in Terrestrial and Marginal Sea Ecosystems of China” (CBTSEC) of Chinese Academy of Sciences (CAS). It is also helpful for enhancing the observing capability of CERN

**Table 1.** The system specification

Aimed compound	CH <sub>4</sub>	CO <sub>2</sub>	N <sub>2</sub> O
Column	Col <sub>1</sub> : SS-2 m×2 mm, packed with 13XMS (60/80 mesh) <sup>a</sup>	Col <sub>2</sub> : SS-2 m×2 mm Packed with Porapak Q (60/80 mesh)	Col <sub>3</sub> : SS-1 m×2 mm; packed with Porapak Q (80/100 mesh) Col <sub>4</sub> : SS-3 m×2 mm; packed with Porapak Q (80/100 mesh)
Carrier gas/flow rate (cm <sup>3</sup> min <sup>-1</sup> )	N <sub>2</sub> (99.999%) /30	N <sub>2</sub> (99.999%)/25	N <sub>2</sub> (99.999%)/25
Oven temp. (°C)	55	55	55
Converter/ temp. (°C)	—	Nickel catalyst/375	—
Detector/temp. (°C)	FID/200	FID/200	ECD/330
Air & H <sub>2</sub> flow rate (cm <sup>3</sup> min <sup>-1</sup> )	Air, 400 H <sub>2</sub> , 30	Air, 400 H <sub>2</sub> , 30	— —
Retention time (min)	1.75	1.4	3.5
Range	0.95–60.6 ppmv	195–4020 ppmv	163–9412 ppbv
Accuracy <sup>b</sup>	± 32 ppbv	± 1.29 ppmv	± 5.0 ppbv
Responsible factor (RF)	0.00032 ppmv	0.00047 ppmv	0.069 ppbv <sup>c</sup> 0.093 ppbv <sup>d</sup>
Flux detect limit <sup>e</sup>	0.062 mg m <sup>-2</sup> h <sup>-1</sup>	6.89 mg m <sup>-2</sup> h <sup>-1</sup>	0.027 mg m <sup>-2</sup> h <sup>-1</sup>

<sup>a</sup> Material-length×inner diameter; Packing material (mesh); SS-Stainless Steel

<sup>b</sup> Concentrations are CH<sub>4</sub> 2.02 ppmv, CO<sub>2</sub> 524 ppmv, and N<sub>2</sub>O 333 ppbv.

<sup>c</sup> Low concentration spanning 333–2753 ppbv

<sup>d</sup> High concentration spanning 3362–9412 ppbv

<sup>e</sup> Pressure: 1000 hPa, temperature: 298 K, chamber height: 50 cm, exposure time: 10 min

to install the system on 16 research stations.

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