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AUTOMATED GAS SAMPLING SYSTEM FOR LABORATORY ANALYSIS OF CH$_4$ AND N$_2$O[†]

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ABSTRACT

Analyzing the flux of CH$_4$ and N$_2$O from soil is labor intensive when conventional hand injection techniques are utilized in gas chromatography. An automated gas sampling system was designed and assembled from a prototype developed at the National Soil Tilth Laboratory in Ames, IA. The sampler was evaluated for accuracy and precision when attached to a Varian[1] 3700 gas chromatograph configured with flame ionization and

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[1]Mention of commercial products in this paper is solely to provide specific information for the reader. It does not constitute endorsement by the USDA's Agricultural Research Service or the University of Nebraska's Agricultural Research Division over other products that may be suitable.

electron capture detectors. The automated gas sampling system is easy to operate and provides acceptable results (standards ranging from 1.0–5.0 ppmv CH_4 and 0.342–2.0 ppmv N_2O had coefficients of variation ranging from 1.7–5.6%) while providing an economical approach for analyzing large numbers of gas samples with minimal labor and equipment cost.

INTRODUCTION

Quantifying trace gas fluxes from terrestrial ecosystems to address current concerns about global climate change can generate a large number of samples. Manual injection techniques (either with a syringe directly onto the column or into a sample loop) have traditionally been used, in conjunction with gas chromatography and the appropriate detector, to measure greenhouse gas concentrations. Increased interest in the assessment of the role of soils in the production or consumption of trace gases will likely lead to increased sample loads. Automated procedures which reduce labor costs and increase sample output are needed.

The electron capture detector (ECD) traditionally has been used to measure ambient levels of N_2O (315 ppbv) (1) and the flame ionization detector (FID) for ambient levels of CH_4 (1.75 ppmv) (2). Configuring a gas chromatograph (GC) with ECD and FID detectors and an automated gas sampling system (AGSS) was an obvious approach.

The AGSS used in this method has two modifications that were not published in Parkin's (3) original design. The AGSS designed by Parkin (3) relied on the pressurized gas in vials to propel flow through the tubing and fill a sample loop. System component timing and trouble shooting were difficult and time consuming. Design modifications for our system included the addition of an automated gas sampling syringe, that mechanically draws samples from vials, and light emitting diodes (LED) that are visual aids in trouble shooting and the sequential timing of program controlled components.

The objectives of this paper were to describe the design and assembly of an AGSS that is reasonably priced, reduces labor costs, and maintains an acceptable level of accuracy and precision.

MATERIALS AND METHODS

AGSS Construction

The AGSS design for automated analysis of CH_4 and N_2O was constructed and tested at the USDA-ARS Soil and Water Conservation Research Laboratory at

the University of Nebraska in Lincoln (Fig. 1). A 386 computer, with Q Basic software (program listed in Table 1), signals an A/D converter that opens and closes relays to control the AGSS components. Pneumatic solenoids controlled by the relays are used to control compressed air flow $(4.2\,kg\,cm^2)$ to and from pneumatic cylinders. These cylinders are either attached to or built into different components of the system to perform the tasks necessary to extract a sample from a sealed vial and split the sample into two separate sample loops $(1\,cm^3)$. The samples are then diverted to the appropriate detectors after which a purge valve opens to flush the previous sample from the lines and then closes. Relays are also used to advance a fraction collector and start and stop integrators. The components used to construct the AGSS and their manufacturers are listed in Table 2.

  The AGSS is independent of the specific analytical instrumentation, but in this study a Varian[1] 3700 GC equipped with dual columns (two 3-m long $\times 0.0032$-m O.D. stainless steel tubing; packed with 80/100 mesh porapak N for CH_4 analysis and 80/100 mesh porapak Q for N_2O analysis) and dual detectors was used. The columns and detectors were operated at 75° and 270°C, respectively. Nitrogen was used as the carrier gas $(60\,cm^3\,min^{-1})$ for the ECD while He was used as the carrier gas $(30\,cm^3\,min^{-1})$ for the FID. Retention times for CH_4 and N_2O were 0.54 and 1.32 min, respectively.

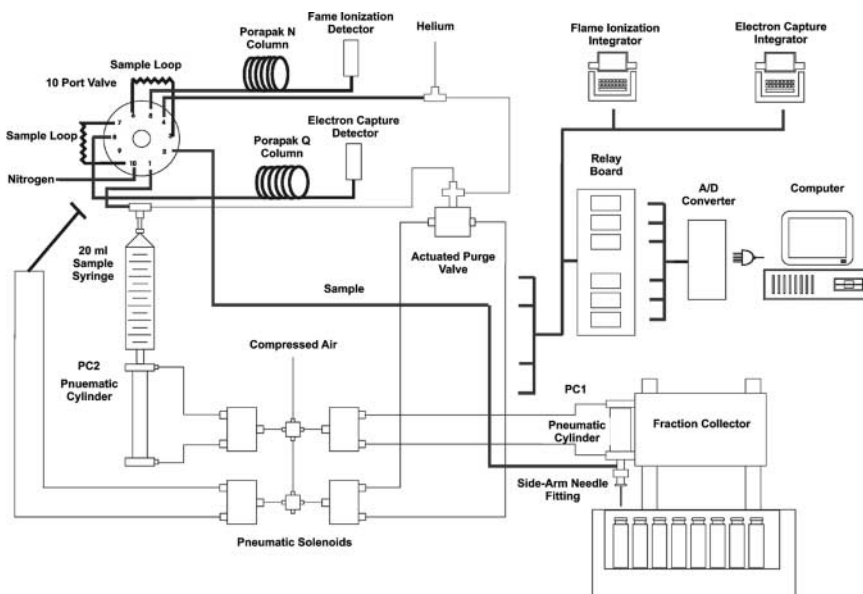*Figure 1.*   Automated gas sampling system.

Table 1. A Basic Program for the Automated Gas Sampling System

Line	Command	Description
1000	OPEN "COM1:9600,N,8,2,CS,DS" FOR RANDOM AS 1	Opens RS232 as a file
1100	PRINT #1, CHR$(64);	Send command turns relays 1–6 off
1200	PRINT #1, CHR$(192);	Send command turns relays 7–12 off
1220	FOR a = 1 TO 100000: NEXT	Brief time delay
1300	PRINT #1, CHR$(66);	Open 10 port valve (relay-1) open purge valve (relay-2)
1310	FOR a = 1 TO 10000: NEXT	Brief time delay
1320	PRINT #1, CHR$(70);	Actuates sample syringe (relay-3)
1325	FOR a = 1 TO 10000: NEXT	Brief time delay
1400	PRINT #1, CHR$(72);	Close Purge valve (relay-2) and push needle into septa (relay-4)
1410	FOR a = 1 TO 10000: NEXT	Brief time delay
1500	PRINT #1, CHR$(76);	Pull sample from septa (relay-3)
1510	FOR a = 1 TO 10000: NEXT	Brief time delay
2000	PRINT #1, CHR$(77);	Direct Sample to GC (relay-1)
2100	PRINT #1, CHR$(93);	Turn Integrator on (relay-5)
2200	PRINT #1, CHR$(85);	Remove Needle from septa (relay-4)
2210	FOR a = 1 TO 10000: NEXT	Brief time delay
2300	PRINT #1, CHR$(64);	Move syringe back up (relay-3)
2310	FOR a = 1 TO 10000: NEXT	Brief time delay
2400	PRINT #1, CHR$(193);	Move auto sampler (relay-7)
2410	FOR a = 1 TO 10000: NEXT	Brief time delay
2500	PRINT #1, CHR$(192);	Turn auto sampler off
2510	FOR a = 1 TO 1000000: NEXT	Delay to allow Chromatographs to resolve (2 min and 20 sec)
2515	PRINT #1, CHR$(96);	Shut integrators off (relay-6)
2616	FOR a = 1 TO 10000: NEXT	Brief time delay
3000	GOTO 1100	Go back to beginning

Table 2. Laboratory Designed and Assembled Automated Gas Sampling System Parts List

Component	Catalog Number	Vendor	Location	Phone No.	Cost[a]
10 Port Valve with actuator	A10UWE	Valco Instruments	Houston, TX	800-367-8424	$600
Retriever IV Fraction Collector	68-2260-001	ISCO Inc.	Lincoln, NE	402-464-0231	$2,995
Pneumatic Cylinder[b]	Aurora HB12 1″ Bore x1″ Stroke, 5/15″-24-5/8″ w/Shock Pads	Skarda Hydraulic and Pneumatic	Omaha, NE	800-228-9750	$50
Side-Arm Needle Fitting	6082 (Modified)	Popper and Son, Inc.	New York	516-248-0300	$50
Injection Mask[b]	Designed and manufactured	Precision Machine Co. Inc.	Lincoln, NE	402-467-5528	$200
A/D Converter/w serial cable and 9 V DC power supply	ADC-1	Remote Measurement Systems	Seattle, WA	206-328-2255	$630
5 V DC Reed Relay[c]	275-232	Radio Shack	Lincoln, NE	402-467-3301	$3
12 VDC L.E.D.[c]	276-209	Radio Shack	Lincoln, NE	402-467-3301	$1
5 V DC L.E.D.[c]	276-208	Radio Shack	Lincoln, NE	402-467-3301	$1
AC to12 V DC power supply[c]	WP30120N	Condor		708-745-7141	n/a
Solenoid (12 V DC 0–125 psi)	Humphrey 410	Skarda Hydraulic and Pneumatic	Omaha, NE	800-228-9750	$34
Purge valve (Actuator)	Whitney SS-41XS2-51D	Omaha Valve and Fitting Co.	Omaha, NE	800-247-7061	$242

Table 2. Continued

Component	Catalog Number	Vendor	Location	Phone No.	Cost[a]
Purge valve	Whitney Model 131 DA	Omaha Valve and Fitting Co.	Omaha, NE	800-247-7061	n/a
Syringe (Pneumatic Cylinder)	Aurora HB12 3/4″ Bore x3″ Stroke, 1/4″-28-5/8w/Shock Pads	Skarda Hydraulic and Pneumatic	Omaha, NE	800-228-9750	$50

Mention of commercial products in this paper is solely to provide specific information for the reader. It does not constitute endorsement by the USDA's Agricultural Research Service or University of Nebraska's Agricultural Research Division over other products that may be suitable.

[a] Estimated cost of components.
[b] Components added to the Retriever IV Fraction Collector.
[c] Components used to assemble relay board.

AGSS Operation

Rubber-stoppered vials containing the gas sample are positioned on the fraction collector that serves to sequentially position the vials under a pneumatic cylinder (PC1). The push rod of the pneumatic cylinder is fitted with a side-arm needle fitting. At the beginning of a sampling cycle, the sample lines and needle are flushed with He by opening the purge valve and actuating the 20 mL sample syringe several times, to purge the system of any previous sample. The purge valve is then reset and the pneumatic cylinder located over the sample vial is activated, causing the needle to penetrate the vial septum. This operation connects the sample vial with the 10 port sample valve containing the two sample loops. A gas sample is introduced into the sample loops by means of a second pneumatic cylinder (PC2) attached to the 20 mL sample syringe. Activating the solenoid connected to the pneumatic cylinder causes the sample syringe to alternately draw a sample through the connecting lines and into the sample loops. The 10 port valve is actuated, bringing the gas in the sample loops in-line with the He and N_2 carrier gases. After the sample gas is swept into the columns, the 10 port sample valve is reset, the needle is removed from the sample vial, the fraction collector advances to the next vial, and the system waits until analysis of the first sample is complete.

AGSS Evaluation

The precision and accuracy of N_2O and CH_4 detection using the AGSS, interfaced with a Varian[1] 3700 GC was evaluated by analyzing gas samples collected from a winter wheat field and use of certified gas standards (Scott Specialty Gases[1]).

A vented chamber (59-cm high $\times$ 76-cm diam.) made of stainless steel was inserted (2.5 cm) into the soil of a fall planted winter wheat field. The chamber was closed with a lid, (septa inserted in the top of lid) and sixteen samples (each 20 cm^3 in size) were sequentially collected at one time, using a 20 mL polypropylene syringe fitted with a 25 gauge needle. The samples were immediately transferred into evacuated 10 mL autosampler vials (Wheaton[1] Cat. Log No. 223696) sealed with lyophilization stoppers (Wheaton[1] Cat. Log No. 224100-193) and aluminum seals (Wheaton[1] Cat. Log No. 224178-01). The lid was removed after the time 0 sampling and livestock manure was added (42 t ha^{-1}) to the chamber. The lid was placed back on the chamber and 16 additional samples were collected 7 h later. The lid was removed after the 7 h sampling and water added (11.5 L deionized H_2O). The lid was placed back on the chamber and another 16 samples were collected after 46 h. One-half of the time 0, 7 and 46 h samples collected, were analyzed using a manual injection

technique at the Soil, Plant, and Nutrient Research Unit in Fort Collins, CO while the other half were analyzed using the AGSS at the Soil and Water Conservation Unit in Lincoln, NE.

In addition, eight replicates of three standard gas (Scott Specialty Gases[1]) concentrations for N_2O (0.342, 1.0, and 2.0 ppmv) and CH_4 (1, 2, and 5 ppmv) were consecutively analyzed from the lowest to the highest concentrations, using the AGSS at the Soil and Water Conservation Research Unit in Lincoln, NE. The N_2O and CH_4 standards were prepared for analysis by evacuating the 10 mL vials and adding 20 mL each of the N_2O and CH_4 standard gases (Scott Specialty Gases[1]) to the vials.

Statistical analysis of automated measurements were compared with certified gas samples using a student t test (4).

RESULTS

For the AGSS to be a useful alternative to hand injection methods, it must meet three requirements. First, mean values obtained from repetitive injections of calibration standards must be repeatable. Similarly, typical field sampling ranges must yield the same precision as a method that is assumed to be a standard. Secondly, CH_4 and N_2O concentrations must be determined with accuracy. Third, there must be a demonstrated economical advantage to justify the cost associated with building and operation of the system.

In answering the first requirement, certified calibration standards (Table 3), repetitively injected using the AGSS, resulted in acceptable coefficients of variation for N_2O (2.0–5.6%) and CH_4 (1.7–3.6%). Field samples (Table 4) analyzed for CH_4 indicated the coefficients of variation for the AGSS (1.9–3.4%) were somewhat higher than the manual technique (0.5–1.3%). Coefficients of variation for N_2O using the AGSS (1.7–13.6%) were higher than for the manual injection technique (1.1–1.8%). The GC configuration used in the manual injection has a separate switch valve to divert O_2, away from the ECD (5). Parkin (3), also used a split column backflush configuration for N_2O analysis. Without diversion of the large O_2 peak, sample overloading occurs creating a large broad tailing peak that reduces the analytical precision of N_2O analysis (5). The 13.6% coefficient of variation that was recorded for ambient levels of N_2O for the AGSS is a result of such overloading. Certified standard gases containing N_2O are made up with a balance of N_2. The fact that analytical precision for a 0.342 ppmv standard decreased to 5.6% coefficient of variation supports O_2 tailing as a cause of reduced sensitivity.

To satisfy the second requirement, both CH_4 (Fig. 2) and N_2O (Fig. 3) individual data points for the AGSS and the manual injection system were correlated. The slope for both were 1.0. In addition, linear coefficients of determination were $r^2 = 0.97$ for CH_4 and $r^2 = 1.0$ for N_2O, which indicated good

Table 3. Comparison of Certified Gas Standards of Nitrous Oxide and Methane with Consecutive Measurements

Standards[b]	Nitrous Oxide[a]			Methane[a]		
	0.342 ppmv	1.00 ppmv	2.00 ppmv	1.03 ppmv	2.05 ppmv	5.09 ppmv
	0.332	1.019	2.033	1.01	2.07	5.26
	0.321	1.015	1.980	1.04	2.01	5.00
	0.313	1.013	1.991	1.01	2.10	5.13
	0.332	1.012	1.970	1.11	1.97	5.16
	0.347	1.012	1.914	1.04	2.04	5.03
	0.346	1.049	1.983	1.04	2.04	5.00
	0.297	1.021	1.914	1.11	1.97	5.10
	0.306	0.970	1.971	1.07	2.10	5.07
Mean	0.324[c]	1.014[d]	1.969[d]	1.053[d]	2.039[d]	5.094[d]
SD	0.018	0.021	0.04	0.038	0.052	0.088
CV, %	5.6	2.2	2.0	3.6	2.5	1.7

[a] Consecutively injected Scott Specialty Gases[1] certified value ±5%.
[b] Average integrator readings for each gas concentration were used to develop calibration curves.
[c] Significant at the 0.1 probability level.
[d] Significant at the 0.05 probability level.

Table 4. Comparison of an Automated Gas Sampling System vs. Manual Injection for Methane and Nitrous Oxide Using Sample Vials

Sampling Time (h)	Methane		Nitrous Oxide	
	AGSS[a] (ppmv)	Manual Injection[a] (ppmv)	AGSS (ppmv)	Manual Injection (ppmv)
0	3.61 (3.0)[b]	3.73 (0.8)	0.344 (13.6)	0.348 (1.8)
7	2.28 (1.9)	2.36 (1.3)	1.092 (4.9)	1.046 (1.8)
46	3.10 (3.4)	3.22 (0.5)	6.462 (1.7)	7.053 (1.1)

Values presented are means of field repetitions.
[a] Numbers in parentheses are coefficients of variation (%).
[b] AGSS samples were analyzed at the USDA-ARS-SWCRU Laboratory at the University of Nebraska, Lincoln. Manual injection samples were analyzed by USDA-ARS-SP and NR Laboratory at Fort Collins, Colorado.

agreement between methods. In addition, certified gas standards (Scott Specialty Gases[1]) for CH_4 and N_2O were statistically compared with analysis values using the t test (Table 3). All AGSS measured valves for CH_4 and N_2O, except N_2O at 0.342 ppmv, did not differ significantly ($p < 0.05$) from the certified standards.
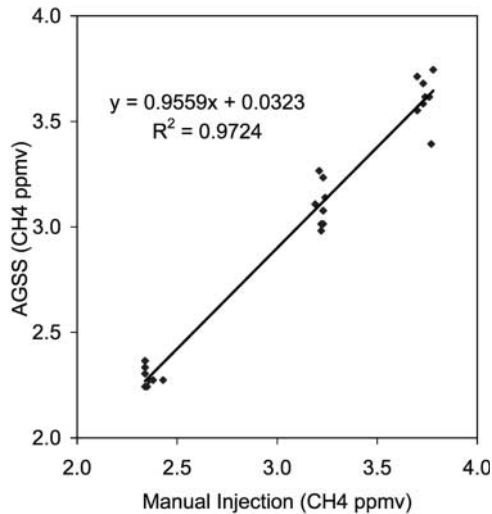

$$y = 0.9559x + 0.0323$$
$$R^2 = 0.9724$$

Figure 2. Comparison of AGSS with manual injection for methane.

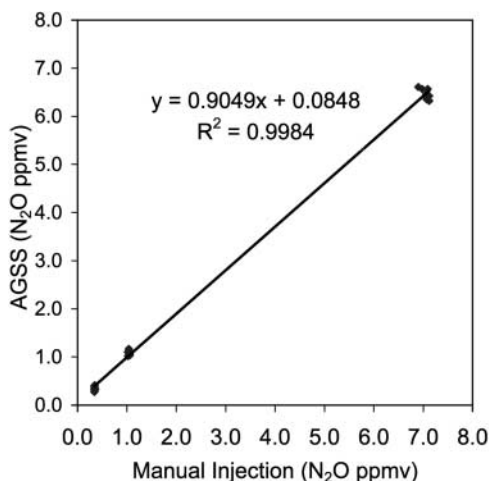$$y = 0.9049x + 0.0848$$
$$R^2 = 0.9984$$

Figure 3.   Comparison of AGSS with manual injection for nitrous oxide.

To justify the cost of building the AGSS, analytical laboratories were assumed to have already in place a GC and integrators capable of analyzing CH_4 and N_2O. In addition, it was assumed a computer with a minimum 386 processing ability is available. The cost of components to build the AGSS was <\$6000. The labor required to analyze 1,500 samples at the Soil and Water Conservation Research Unit at Lincoln, NE, was reduced from 300 h to 150 h using the AGSS.

A sampling device of the same design has been in service since 1990 at the National Soil Tilth Laboratory, Ames, Iowa, and has facilitated the analyses of in excess of 30,000 gas samples. The only required maintenance during this period has been the periodic replacement of the plastic sample syringe (approximately twice/year) and two of the four solenoid valves.

DISCUSSION

The increased interest in global warming and the quest to quantify the soil–atmosphere exchange of greenhouse gases will facilitate the continual development of the AGSS. The AGSS designed and assembled from a prototype built by Parkin (1) includes the addition of a 20 cm^3 syringe that draws the sample out of the sealed vial and into the sample loops.

The Soil and Water Conservation Research Analytical Laboratory added a light emitting diode to each relay. The LED made it easier to determine which of the AGSS components were activated during program timing. The A/D

converter, 10 port valve, actuated purge valve, solenoids, relay board, and syringe were compartmentalized on a 75 cm × 45 cm board.

Gas sampling using an evacuated sealed vial is a very quick and easy approach for collection, storage and analysis of gases. Temperature and atmospheric pressure differences are compensated for when field samples and calibration standards are placed in the vials at the same time under the same conditions.

Alternate uses of the AGSS include real time analysis of gases produced in soil, sediment, water samples, or small pieces of organic materials contained in sealed vials. The incubation of sample material in vials placed directly on the autosampler eliminates the need for transfer of gas samples to a separate vial. This configuration has been used to measure N_2O in the determination of denitrification rates associated with earthworm casts, plant residue, small pieces of organic material, and the soil lining earthworm burrows (6,7), as well as CH_4 production rates associated with groundwater, buried sediments, and wood fragments (8) and the CH_4 production and oxidation activities associated with surface soils (9,10).

CONCLUSIONS

Increased demands for the analysis of soil–atmosphere exchange will facilitate the development of new technology and the improvement of existing technology. Configuring a gas chromatograph as described in this manuscript with the AGSS, will provide scientists with a precise, accurate and economical approach to automation. The system can be easily modified to analyze not only CH_4 and N_2O simultaneously but also CO_2. Adding backflushing to electron capture detection will improve accuracy and sensitivity. The AGSS is very flexible and can be used for many different applications.

ABBREVIATIONS

GC, gas chromatograph; ECD, electron capture detector; FID, flame ionization detector; AGSS, automated gas sampling system; LED, light emitting diodes

ACKNOWLEDGMENTS

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