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An automated technique for sampling the contents of stoppered gas-collection vials*

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Summary We have built an autosampler system that delivers the contents of pressurized gas collection vials to the injection port of a gas chromatograph. The three-part system consists of a shuttle base upon which vials move sequentially past a static sampling point, a sampling needle that is driven through vial septa by an air-driven piston, and an air-actuated sample valve that alternately places a sample loop in line with either a sample delivery line from the sample needle or a carrier stream leading to the gas chromatograph. We have used the system to analyze several thousand gas samples taken from soil cores assayed for denitrification activites, and have found the system reliable and capable of producing highly repeatable results.

Introduction

Experimental studies of biological N_2-fixation, denitrification, soil respiration and other biological processes with important gas-phase components increasingly use gas chromatography to identify and quantify gaseous substrates and products. Refinements in column packings and detection systems have been steady, but have outpaced similar progress in sample delivery systems: there is at present no commercially-available alternative to manual injections of collected gas samples. Single experiments often produce hundreds of samples requiring GC analysis, and in the absence of an automated method for transferring collected gases to the injection port of a GC, a substantial amount of time and expense must be devoted to manual analyses. In our denitrification work, for example, retention times and column backflushings dictate sample injection intervals of $\geqslant 5$ minutes, so that a moderate-sized 500-vial sample set can require > 40 h of analysis. Because immediate operator attention is required only for the *ca.* 30 s sample injection and backflush activation period, the work is tedious and represents an inefficient use of time; automation could both relieve the necessity for a full-time operator and potentially increase injection reliability.

We describe in this note a gas autosampler system that is designed to transfer headspace samples from gas collection vials to the injection port of a gas chromatograph. The system described has been in daily use since July 1983; it is largely self-contained, reliable, and relative to the expense of a full time operator, cost-effective.

Materials and methods

Design

The basic autosampler consists of three major components attached to a single-column single-detector gas chromatograph: 1) a shuttle base upon which upright sample vials are moved about at time intervals, 2) a pneumatic piston that drives a hypodermic needle through vial septa, and 3) a 6-port pneumatically-driven valve which aligns a sample loop with either the

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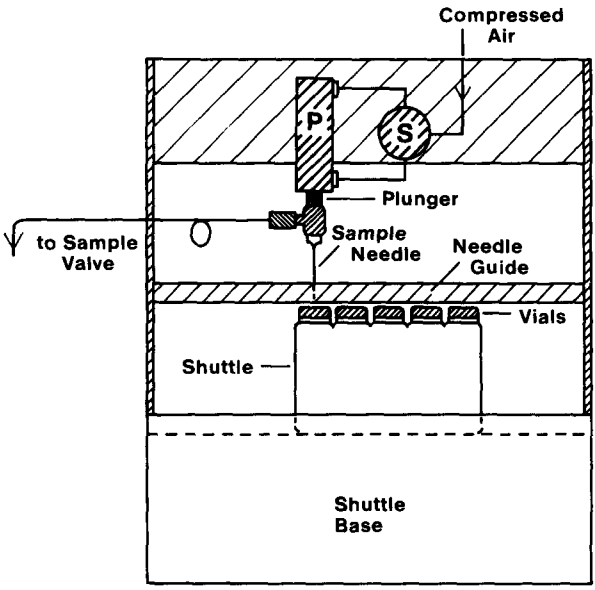

Fig. 1. Autosampler for gas collection vials. Shuttle base is a modified fraction collector; after vial in shuttle moves to beneath the sample needle, the *solenoid* (S) directs compressed air to the *pneumatic piston* (P) to drive the needle through the needle guide and the vial septum into the vial. After the piston retracts the needle from the vial, the delivery line is flushed with carrier gas. Shuttle movement and solenoid are controlled by a sample event control module (SECM) attached to the integrator. We mounted a second piston and delivery line adjacent to the first to make use of a second GC detector and thus double the rate of sample analysis.

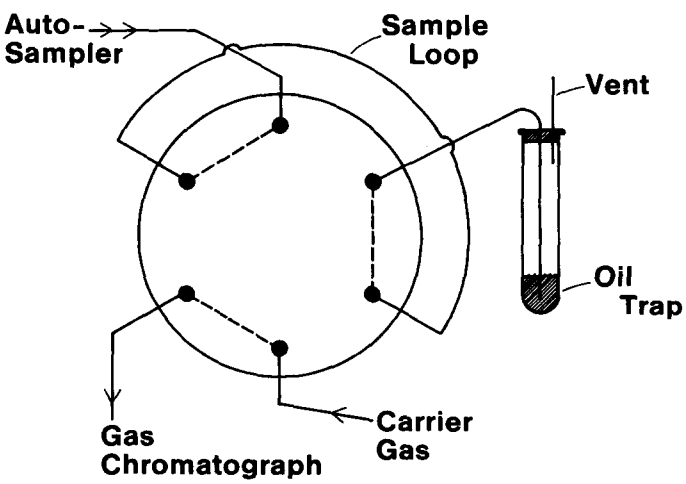

Fig. 2. Autosampler sample valve configuration in fill mode. In injection mode the sample loop is aligned with the carrier stream. See text for description of a possible backflush arrangement.

hypodermic needle or the carrier gas stream (Figures 1 and 2). An optional backflush valving arrangement as described in Parkin *et al.*[1] could both decrease the time required between samples and allow a dual-column arrangement in which the carrier stream passes through one sample loop plus one column to the detector while a backflush stream pushes long-lived extraneous peaks back through an alternate column to a vent.

The shuttle base can be fashioned from any fraction collector that allows external control of shuttle movement. We have removed the drip tower from an Isco (Lincoln, Nebraska, USA) Model 1200 collector and inserted spacers (plastic syringe bodies) in the shuttles to accomodate gas collection vials of a narrower diameter than standard fraction collection tubes. At intervals defined by a sample event control module (SECM), all shuttles progress past the hypodermic needle one vial at a time until the last shuttle disengages the fraction collector drive motor and signals the external module that all vials have been sampled.

The pneumatic piston (Schrader Miniature Cylinder, Scoville Fluid Power Division, Wake Forest, North Carolina, USA) is controlled by a 3-way solenoid (Humphrey Products, Kalamazoo, Michigan, USA) in turn controlled by the SECM. Compressed air entering the solenoid is directed by one of two pathways to the piston; in one solenoid position the plunger is retracted and in the other, extended. To the end of the plunger is attached a 3-way luer-lock stopcock (Perfektum, Popper and Sons Co., New Hyde Park, New York, USA); the stopcock is a convenient means for attaching the needle to the plunger without blocking gas flow between the needle and the sample loop. A 2 cm thick aluminium bar acts as needle guide: during piston extension, the plunger pushes a 25 guage (0.5 mm outside diameter) deflected point needle through a 1 mm hole in this bar and into and through the rubber septum capping a vial. The bar also allows the needle to be extracted from the vial by providing a barrier that keeps the vial from remaining attached to the needle when the plunger is retracted.

A length of nylon tubing (0.5 mm inside diamter × *ca.* 50 cm long) connects the plunger stopcock to the sampling loop inlet. In fill mode (Fig. 2), the other side of the sample loop is attached to a 28 guage (0.36 mm outside diameter) needle immersed in an oil-filled gas trap that allows overpressure within the delivery system to vent slowly to the atmosphere. In inject mode, the sample loop is in line with the carrier stream and the sample is swept to the column. The 6-port valve (Valco Instruments Company, Houston, Texas, USA) is driven by a pneumatic actuator (Valco Helical-Drive Model) and is controlled by another 3-way solenoid switched by the SECM. The sample loop and delivery line are flushed between vials when the sample loop returns to the fill mode (Fig. 2): pre-column carrier pressure (*ca.* 100 kPa [15 psi]) is higher than atmospheric pressure, so that when the carrier-pressurized sample loop realigns with the autosampler, carrier gas is vented through both the sample needle and vent on either side of the sample loop. Because the downstream gas trap is oil rather than water filled, the pressure head at each of the two ends is equal. Several inject and fill cycles are usually needed to completely flush the delivery and vent line; immediately after peaks of interest have passed the detector, our SECM activates a 30-second series of 6 inject-fill cycles before the next vial is sampled. This flushes our 1.1 ml delivery and vent line with *ca.* 6 ml of carrier gas.

Operation

We use a computing integrator (Hewlett Packard Model 3390A) with the companion SECM (Hewlett Packard Model 19400A) to control the activities of all devices. At the start of a sample run the shuttle mechanism moves a previously overpressured vial into position beneath the needle guide, the plunger drives the needle into the vial, and gas from the vial flows through the nylon tubing to the sample loop and gas trap. After the sample loop reaches atmospheric pressure, the sample valve actuator injects the loop contents into the carrier stream; shortly thereafter the autosampler plunger retracts the sample needle from the vial. When the peaks of interest have swept past the detector, the integrator prints the injection report and the sample valve realigns with the autosample delivery line and flushes the line by quickly cycling through several fill-inject cycles. In a backflushed system these flushes would be made using the backflush rather than the carrier stream. After contaminant peaks have swept past the detector,

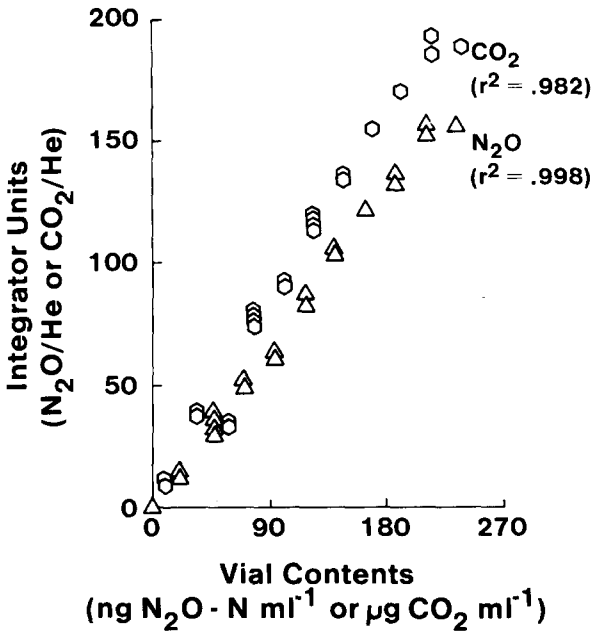

Fig. 3. Data from autosampler run of 38 mixed N_2O and CO_2 standards using He as overpressure and internal standard gas. Overpressured vials without internal standard yield similar results.

the cycle restarts. The final, flagged shuttle causes the fraction collector to send a signal to the integrator to stop the autosample cycle.

Sample vials can be overpressurized with either additional sample or an internal standard gas; we recommend the latter when vials are to be stored for long periods or when chromatographic conditions are likely to change over the course of a several-hour autosample period. Vials to be overpressured by non-sample gas can be pressurized by the autosampler, either immediately after gas samples are collected or immediately before analysis. In the latter case, a second piston-driven needle attached to a gas cylinder and flow meter can be used to inject a set amount of gas into each vial before a given vial reaches the sample needle. Alternately, the overpressure gas line can be substituted for the sample delivery line and vials can be filled in sequence before a sample run.

The amount of gas needed to overpressure a vial will depend on vial, delivery line, and sample loop volumes; we have found that 2 ml of internal standard added to a 3 ml sample vial near atmospheric pressure is adequate to fill our 1.6 ml delivery line and sample loop without diluting sample concentrations below detection limits. Vials containing standards should be overpressured in the same manner as sample vials.

Results

Figure 3 shows results from a single autosampler run using samples of known concentration. Three ml sample vials (Venoject blood collection tubes, Terumo Medical Corporation, Elkton, Maryland, USA) containing known concentrations of CO_2 and N_2O were overpressured with 2 ml of He and placed on our 76 vial autosampler. At the beginning of each injection cycle each of two sample plungers delivered gas samples from two separate vials to independent

injection loops; each loop was aligned with its own column leading to one of two ^{63}Ni electron capture detectors. The carrier streams (95% Ar, 5% C_2H_4) swept through 3 m Porapak Q columns mounted in a Varian 3700 gas chromatograph. Oven temperature was 55°C. Makeup gas of the same composition as the carrier joined the *ca.* 6 ml min^{-1} carrier stream immediately before the detectors to create a flow past the detectors of *ca.* 20 ml min^{-1}. An automatic valving system backflushed these columns after the N_2O peaks.

Simultaneous signals from the two detectors were integrated by the plotting integrator described above and an identical slave unit that was not used to control external events. Both integrators sent their reports to the input port of a microcomputer. Using our double-injection system we routinely analyze 16 sample vials per hour for N_2O and CO_2. Sampling speed is mainly a function of peak retention times.

We have found this autosampler to give highly repeatable results and to be a reliable and cost-effective system. The flexibility with which the system can be implemented and the ready availability of component parts are especially attractive features of the design. Parkin[2], for example, describes a similar autosampler with different equipment and features. He uses an inexpensive Sinclair/Timex microprocessor for event control, has a separate sample loop-needle flush valve, and uses a two-column, single detector arrangement to increase the rate of sample analysis. Other laboratories with large numbers of gas samples to process may also find an autosampler a useful investment.

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Reference

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