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A NEW GAS SAMPLING DEVICE FOR GAS CHROMATOGRAPHY

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SUMMARY

This paper describes a new sampler for taking gaseous samples for gas chromatographic analysis. The device provides samples of precise and selectable volume and can be used in place of conventional sampling valves. It has an advantage over conventional samplers in that it has no moving parts in the sample path. It can be constructed in any material that can be made in the form of pipes, this includes silica, glass, gold etc., so that it is suitable for labile compounds. The only moving part in the system is a two-way valve remote from the sampler and in the carrier gas supply. The design is such that the sample size is not sensitive to the temperature of the sampler, consequently the sampler can be used in high and variable temperature situations such as inside furnaces and reaction vessels.

The sample size is selected remotely through a timer. This permits easy change of sample size and calibration of the gas chromatograph. The principles of operation and the mathematical theory are developed to show the theoretical limits within which precise repeatable samples can be taken. Experimental results are presented to show good agreement with the theory and to illustrate that the precision of sampling under a variety of conditions is as good or better than modern gas sample valves.

INTRODUCTION

Gas sampling valves are widely used for introducing gaseous samples into gas chromatographs. While these perform reasonably well, they have a number of limitations and the full potential of introducing a precise volume of gaseous sample into a column is not usually realised.

Some of the limitations arise from the basic design, where a fixed volume of tube (or groove) is isolated at each end to contain the gaseous sample, before it is diverted to the column. The amount of sample isolated (number of molecules) is necessarily sensitive to both the temperature and the pressure in the volume. For precise quantitative work both temperature and pressure must be controlled. More severe problems are caused by the mechanical means of isolating the ends of the fixed volume and diverting the flow. These moving parts have to withstand the temperature, pressure and corrosiveness of the sample, at the same time making a perfect and repeatable seal. In addition, the sampling valve must produce, as nearly as pos-

sible, an undiluted sample plug with sharp front and back edges. Any unswept volumes or sharp corners are likely to cause bad sample profiles. It is not surprising that gas sampling valves sometimes fail and that there are considerable constraints on the circumstances under which they can be used.

The idea of a gas sampling device based on pressure balance flow switching principles is attractive. It should be possible to avoid moving parts in the sample path and to define the sample size by time rather than mechanical volume. This paper describes the design and performance of such a device.

Design

Early experimental work was based on heartcutting and column switching systems previously published^{1,2}. Some other (unpublished) flow switching schemes were also tried, including fluid logic devices, but they all suffered to some extent from poor repeatability of sample size or sensitivity to sample temperature.

Fig. 1 shows the flow diagram of the new system³.

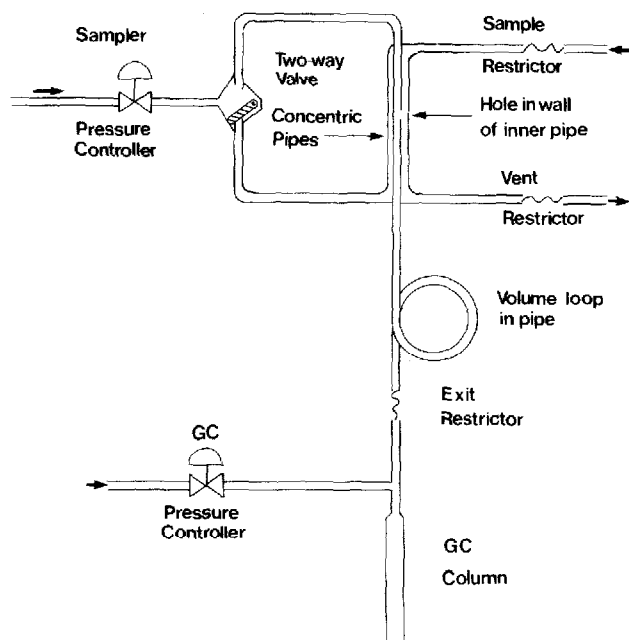


Fig. 1. Flow diagram of sampling device.

The system is set up so that the gas chromatograph inlet pressure controller operates normally at the desired column head pressure, the sampler pressure controller is set to about 5 p.s.i. (0.3 bar) higher. There are three restrictors in the gas flow system, the vent restrictor, the sample restrictor and the sampler exit restrictor. Their values are not critical except that, under operating conditions, the rate of flow through each should be in the order

$$\text{vent flow} > \text{sample flow} > \text{sampler exit flow} \quad (1)$$

Also

$$\text{gas chromatograph column flow} > \text{sampler exit flow} \quad (2)$$

Suitable restrictors for this purpose can be constrictions in the pipes. Under these conditions, when the two-way valve is in the position shown in the diagram, carrier gas flows from the sampler pressure controller through the upper pipe and down through the sample exit restrictor to join carrier from the column head pressure controller to go to the gas chromatographic column. Some carrier also flows through the hole in the pipe wall to join the flow of sample going out to vent. When the two-way valve is in the other position, the carrier flows through the lower pipe to the bottom of the sampler to join some of the sample going out to vent. As there is no carrier flowing down the upper pipe, undiluted sample flows from the outer pipe of the sampler, through the hole to provide the flow to the gas chromatograph. Excess sample goes past the hole to join the carrier going to vent. By timing the operation of the two-way valve a precise slug of sample can be introduced into the carrier going to the gas chromatograph.

The sample size, number of moles (s), taken is determined by the mole flow-rate (F_h) through the hole and the sample time (t) that the sample is switched to go through the hole.

$$s = F_h \cdot t \quad (3)$$

Assuming that there is negligible pressure drop and change in temperature profile between the sampler body and the sampler exit restrictor during the sample time (0.2 to 10 sec), then F_h will be equal to F_e , the mole flow-rate through the sampler exit restrictor. The mole flow-rate through the sample exit restrictor will remain the same from sample to sample if the pressure and temperature at the sampler exit restrictor remain the same. Change in temperature of the sampler itself should not affect the mole flow-rate. The repeatability of sample size depends on how well the parameters at the sampler exit restrictor are controlled. The flow F_e is given by the equation:

$$F_e = \frac{(P_i^2 - P_o^2)}{R \cdot \mu} \quad (4)$$

where μ is the viscosity of the gas going through the restrictor; R is the pneumatic impedance of the exit restrictor; P_i and P_o are the inlet and outlet pressures across the restrictor.

If we assume that the restrictor is mechanically stable and R remains constant, then the pressures and the viscosity must be kept constant. To keep the pressures constant there must be no change in pressure with change in sample flow or temperature at the sampler. This implies that the resistance to flow from the sampler pressure controller to the exit restrictor is negligible and that there is no internal roughness. Fortunately the duty of the pressure controller is not severe as there is no change in flow demanded when the two-way valve is operated. However, there is an implication that the two-way valve, when it is operated, should not "pump" the carrier gas. The pressure at the outlet side of the sample exit restrictor (P_o) must similarly be kept constant during the sample time. This is controlled by the column head pressure controller.

The viscosity of the gas going through the exit restrictor must be the same during each sample time. Therefore during the sample time the gas going through this restrictor must be pure carrier gas and not sample, also the temperature must be the same at each sample time. This is achieved by introducing a length of pipe with sufficient volume to contain all the sample, between the sampler and the exit restrictor, and by thermostating the restrictor. The sampling device itself can be at a distance from the exit restrictor.

EXPERIMENTAL

Several forms of the sampler have been used with satisfactory results. One of the simplest to make and the one that was used in the experimental work presented here is shown in Fig. 2. It is constructed from 1/8 in. and 1/16 in. stainless-steel pipe and Swagelock couplings.

In order to determine the characteristics of the sampler pure ethane was used as the sample, supplied from a cylinder through a pressure controller. The flow diagram for this work is shown in Fig. 1. The gas chromatograph used a flame ionisation detector and a 2 m \times 2.4 mm I.D. column packed with 100–120 BS mesh Porasil B isothermally at 70°C. The sampler was housed in a separate oven so that its temperature could be altered independently. The sampler exit restrictor was in the chro-

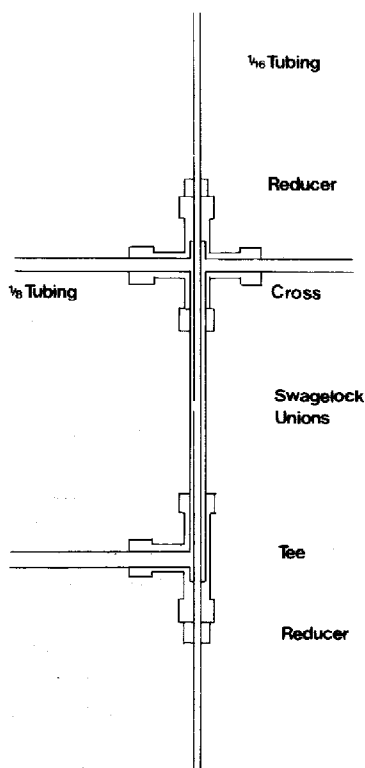


Fig. 2. Construction of sampler.

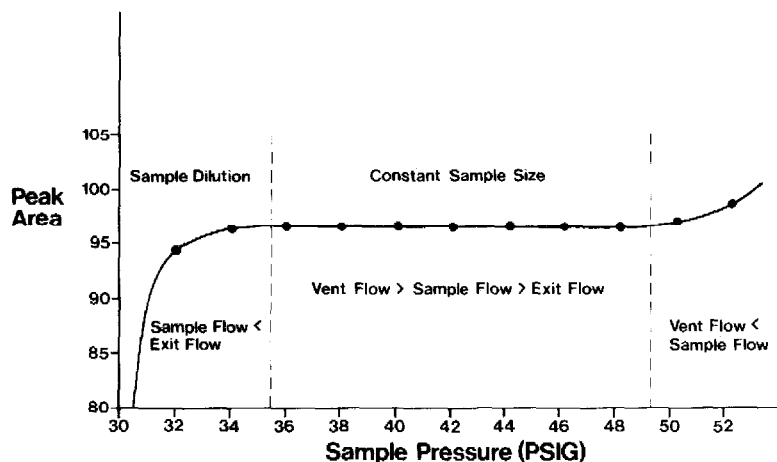


Fig. 3. Effect of variation of sample flow-rate.

matograph oven. Peak areas were measured with a LDC 308 integrator. The sampler was set up with a vent flow of 150 ml/min, a sampler exit flow of 7.5 ml/min with a sampler pressure of 30 p.s.i.g. (ca. 2 bar). The sample time was 2 sec, set by an electronic timer.

The ethane pressure was varied over the range 32–56 p.s.i.g. and a graph of peak area against sample pressure plotted, Fig. 3.

Using a sample pressure of 40 p.s.i.g. a series of eighteen injections of ethane was made, the peak areas are reported in Table I, together with the mean and percent standard deviation.

Similarly, a series of injections was made using different sample times between 0.1 and 5 sec. The peak area for these injections is shown plotted against switch time in Fig. 4.

In order to investigate the sensitivity of the sampler to change in temperature, a series of duplicate injections was made with the sampler temperature held at 50°C intervals over the range 50–400°C. Table II shows these results together with the mean and standard deviation of the peak areas.

Another set of experiments was undertaken using a mixture of *o*- and *m*-xylene continuously vaporised and fed to the sampler as shown in Fig. 5. The sampler was held at 240°C. The sampler exit restrictor and the column head pressure controller were omitted so that the sampler pressure controller served both purposes and the

TABLE I
PEAK AREAS, REPEATABILITY OF ETHANE

9659141	9668541	9658360
9634799	9670698	9666008
9675183	9647072	9660102
9662635	9678893	9648022
9663433	9653870	9666197
9654531	9668324	9636987
Mean = 9659599		Percent standard deviation = 0.12%

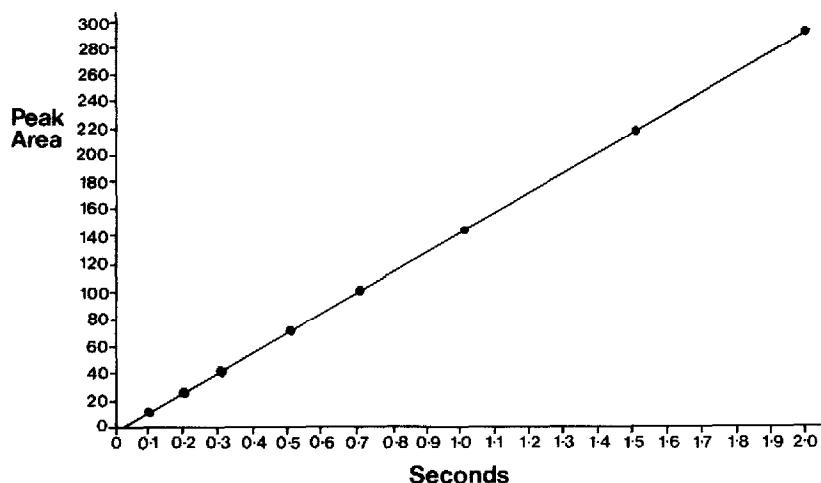


Fig. 4. Sample size as a function of sample time.

column acted as the sampler exit restrictor. The column for this set of experiments was 4 m \times 2.4 mm I.D. packed with 10% bentone 34 plus 5% diisodecylphthalate on 60-80 BS mesh Chromosorb W AW used at 100°C. The results of a repeatability test are given in Table III.

DISCUSSION

Tables I-III show the repeatability of the system under a variety of circumstances. The repeatability figures include the variability of the whole gas chromatograph, integration and in the case of the xylenes, the feed and vaporization systems. In our experience these repeatabilities are as good as, or better than, those obtained using mechanical sample valves.

The graph of peak area against sample time shows that the sample size is exactly proportional to sample time with a small (0.02 sec) dead time (t'). This means

TABLE II

PEAK AREAS OF SERIES OF DUPLICATE INJECTIONS OF ETHANE AT DIFFERENT TEMPERATURES

Temperature (°C)	Peak areas	
50	5449776	5427509
100	5431037	5468000
150	5472006	5485158
200	5494397	5478391
250	5455733	5442827
300	5458616	5443441
350	5440234	5413126
400	5412860	5390571
Mean = 544730	Percent standard deviation = 0.50%	

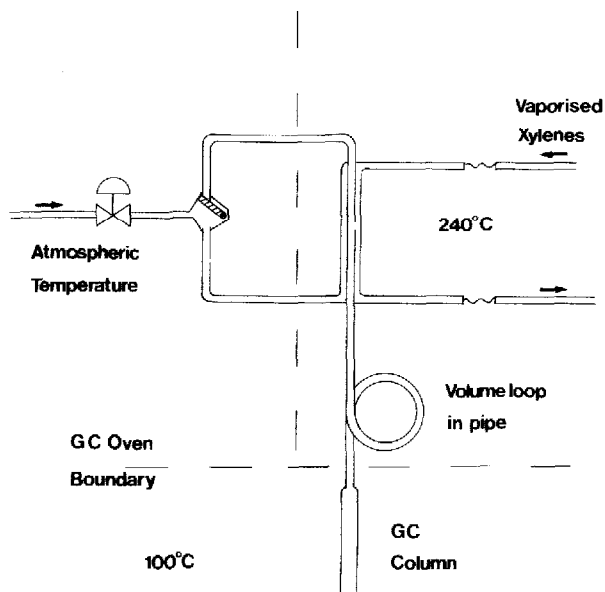


Fig. 5. Flow diagram of simplified application.

TABLE III

PEAK AREAS OF A MIXTURE OF *o*-XYLENE AND *m*-XYLENE

Chromatographic conditions as described in text.

<i>m</i> -Xylene	<i>o</i> -Xylene	Total
5841000	2998400	8839400
5805000	2992700	8797700
5801000	2974200	8775200
5842300	2982100	8824400
5809300	2981200	8790500
5781700	2982300	8764000
5859700	3025800	8885400
5819100	2977400	8796500
5788800	3011300	8800100
5809700	2993100	8802800
5839600	2994800	8834400
5825100	2987100	8812200
5840500	3022000	8862400
5836900	2991600	8828400
5840400	3016300	8856600
5817200	2983500	8800700
5781300	2988500	8768900
Mean		
5819900	2994700	8814000
% S.D.		
0.40	0.52	0.38

that sample size can be selected through the timer with ease and that calibration and linearity checks can be undertaken simply by altering the sample size. The dead time is independent of the nature of the sample (not demonstrated in the results presented). The dead time is the time taken from initiating the operation of the two-way valve until the sample starts to emerge inside the inner tube of the sampler. The dead time (t') depends on the volume flow-rate through the hole (F_h) and the volume of the hole (v):

$$t' = v/F_h$$

Eqn. 3 for moles of sample(s) is better written:

$$s = F_h(t - t')$$

As F_h the volume flow-rate (but not F_h the mole flow-rate) is dependent on the sampler temperature, the dead time is also temperature dependent. It is important that t' is kept small if the sample size is to be essentially temperature independent. F_h is constrained by the maximum rate the gas chromatograph column will accept, therefore t' is minimised by making the volume of the hole as small as possible without creating significant resistance to flow.

That the sample size is independent of the temperature of the device, for the design described is shown by Table II.

The graph of peak area against sample pressure shows a plateau where sample size is independent of sample pressure. At low sample pressure there is insufficient sample flow to match the sampler exit flow to the gas chromatograph so the sample is diluted with carrier, *i.e.* the second requirement of eqn. 1 is not met. At high sample pressure the sample flow becomes equal to the vent flow and sample starts to diffuse into the carrier pipe and ultimately to bleed continuously into the carrier stream. The length of the plateau can be altered to suit the circumstances by adjusting the vent restrictor (or the sample restrictor).

There are two limitations on the situations in which the sampler can be used in its present form. The first limitation is that the sample pressure must be above the gas chromatograph inlet pressure. The second limitation is that there must be sufficient sample available to allow the sampler to operate at least over a period longer than the sample time. The first limitation can be overcome by the use of suitable additional equipment which will be described in another paper. It is, of course, important that neither solids nor entrained liquids get into the sampler.

The sampler has now been used successfully in a variety of applications for both routine and non-routine gas chromatographic analyses. Because it is not sensitive to temperature and can be used in hostile environments it is suitable for taking samples from furnaces, chemical reactors, autoclaves etc. The pipe work for the sampler and its connection to the gas chromatograph can be made from any suitable material that can be formed into pipes. Glass, fused silica, gold, platinum and stainless steel are obvious candidates.

ACKNOWLEDGEMENT

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