

## Note

### Simple modification to compensate for the baseline variation due to the introduction of a reduced-pressure gas sample into a gas chromatograph

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Gas chromatography (GC) is the most convenient method for the analysis of materials such as industrial gases. In most of commercially available gas chromatographs, a pneumatic mass flow controller is used to provide a constant flow of carrier gas. This flow controller has the disadvantage that it is slow to respond to variations in carrier gas pressure<sup>1</sup>. Gas analysis is also widely carried out using a gas chromatograph with a packed column and a conventional gas sampler. The gas sampler is used to introduce the gas sample, which is withdrawn under atmospheric pressure, into the gas chromatograph.

The pressure of the sample gas is not always equal to that of the carrier gas. Therefore, if a sample gas at close to or less than atmospheric pressure is introduced into a gas chromatograph, baseline variations may be found on the chromatogram<sup>2</sup>. This baseline variation, called a ghost peak, becomes progressively greater as the pressure difference between the sample and carrier gas pressures increases. Such a phenomenon is commonly observed on chromatograms obtained by the use of a gas chromatograph equipped with a packed column, a pneumatic mass flow controller and a flow-sensitive detector such as a thermal conductivity detector. In order to avoid such baseline variations, it is usually necessary to reduce further the volume of the sample loop, or to increase the pressure of the sample gas to that of the carrier gas by the use of a special valve<sup>3,4</sup>.

In this paper, we report a new introduction system developed for gas samples at reduced pressures and to reduce the irregular baseline variations on gas chromatograms.

## EXPERIMENTAL

The experiments were carried out using a Shimadzu GC-9A gas chromatograph equipped with a thermal conductivity detector and a computerized integrator (Shimadzu C-R3A). In this gas chromatograph, the carrier gas flows are controlled with pneumatic flow controllers. The sampling and injection system were modified as shown in Fig. 1. This system consists of an ordinary sampling system and a bypass line. The bypass line with a 10 p.s.i. relief valve (NUPRO SS-2C-10) (12) and a 5-ml

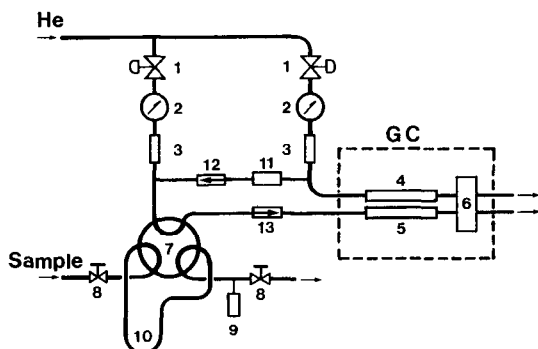


Fig. 1. Schematic diagram of apparatus. 1 = Flow controller; 2 = pressure gauge; 3 = flow meter; 4 = reference column; 5 = analytical column; 6 = detector; 7 = six-port air-actuated rotary valve (Valco Instruments, C-6P); 8 = diaphragm stop valves (Nupro, SS/DLS4); 9 = pressure transducer (Trans Metrics, P-21BA); 10 = sample loop; 11 = surge tank (5 ml); 12 = 10 p.s.i. relief valve; 13 = 5 p.s.i. relief valve.

surge tank (11) was installed between the two carrier gas lines; one is for the analytical (chromatographic) column line and the other for the reference column line. The relief valve (12) can be operated to open the bypass line when the pressure difference between the inlet and outlet of the relief valve is over *ca.* 10 p.s.i.

Additional helium is consequently fed through the bypass line from the reference column line into the sample loop (10); the pressure in the sample loop can be close to and/or equalized to the pressure of the carrier gas. A 5 p.s.i. relief valve (NUPRO SS-2C-5) (13) is installed to prevent suction of the carrier gas into the analytical column during the pressurizing period. In this way, the sample gas can be pressurized quickly, and pressure variations of the carrier gas can be reduced.

The carrier gas helium was prepurified through an oxygen trap column (Applied Research, Oxytrap). A standard gas generator (STEC, SGGU-9000) was used to prepare gas mixtures ranging in concentration from 1 to several tens of ppm; and gas mixtures in cylinders were also used, if necessary. The operating parameters of the gas chromatograph are given in Table I.

TABLE I  
OPERATING CONDITIONS OF THE GAS CHROMATOGRAPH

Parameter	Component	Conditions
Columns	Analytical	MS-5A, 60-80 mesh, 1.5 m × 3 mm I.D.
	Reference	MS-5A, 60-80 mesh, 1.5 m × 3 mm I.D.
Temperatures	Oven	50°C
	Injector	70°C
	Detector	70°C
Thermal conductivity detector		180 mA
Carrier gas (He)	Analytical column	50 ml/min at 1.8 kg/cm <sup>2</sup> G
	Reference column	70 ml/min at 1.9 kg/cm <sup>2</sup> G

## RESULTS AND DISCUSSION

A series of experiments were conducted to assess and demonstrate the effects of this system for the reduction of baseline variations. The 10 p.s.i. relief valve was used in order to open and/or close the bypass line. This relief valve was chosen after considering the pressure drop in the sample loop; it is necessary that additional helium can be quickly fed into the sample loop without overpressurizing. Under the proposed conditions, even if the column length, oven temperature and carrier gas flow-rate were changed, the system could be successfully operated without any modification of the system. As mentioned above, however, it is required that the carrier gas pressure in the reference column line be maintained slightly higher than that in the analytical column line; the pressure difference between the two carrier gas lines was set in the range 0–0.25 kg/cm<sup>2</sup>. As shown in Fig. 2, when a gas sample that was taken into the sample loop (4.47 ml) under atmospheric pressure was introduced into the analytical column using the conventional system, the ghost peak overlapped other peaks of rapidly eluted gases such as hydrogen, oxygen and nitrogen. Consequently, it was difficult to determine their peak areas accurately with the tailing of the ghost peak, even with the use of a computerized integrator. On the other hand, such a large ghost peak did not appear on the chromatogram obtained with the present system, as shown in Fig. 2. The results indicate that the present modified system could be successfully compensate for the large baseline variations on the chromatogram.

The calibration graphs obtained with both systems are shown in Fig. 3. The graphs for methane did not show much difference between the two systems as this peak eluted separately from the ghost peak and there was little interference from the tailing of the latter. On the other hand, the argon peak, which eluted more rapidly, overlapped considerably with the tailing of the ghost peak when the conventional system was used. Therefore, the ghost peak caused a large interference in the measurement of the peak area of argon; the results showed that the calibration graph had a large deviation from the origin. However, the large ghost peak did not appear on the chromatogram obtained with the present system, as shown in Fig. 3. The repro-

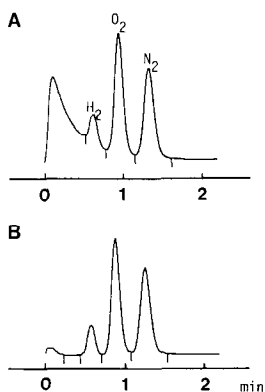


Fig. 2. Gas chromatograms of hydrogen, oxygen and nitrogen obtained with (A) the conventional and (B) the present systems. Sampling pressure: 744 mmHg. GC conditions as in Table I.

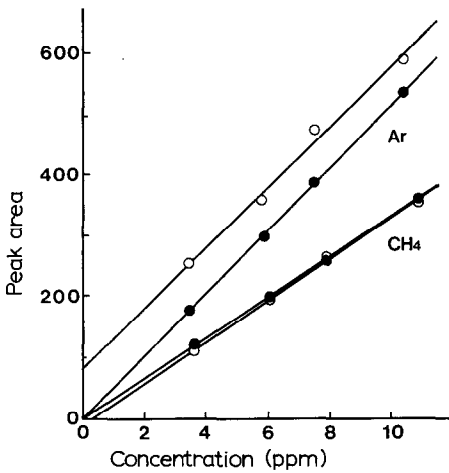


Fig. 3. Calibration graphs obtained with (○) the conventional and (●) the present systems. Sampling pressure: ca. 760 mmHg. GC conditions as in Table I.

ducibility (relative standard deviation,  $n=8$ ) was 2.70% at a level of 4.7 ppm of oxygen in helium and was half of that with the conventional system.

The present system was found to be useful and reliable for the analysis of gas samples, taken under reduced pressure, with a gas chromatograph equipped with a packed column and a flow-sensitive detector such as a thermal conductivity detector.

#### REFERENCES

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