A gas-phase chromatography sample injection device for use with gas samples in the micron pressure range

The analysis by gas-phase chromatography of a gas sample which is present at a pressure in the range 10^{-2}–10^{-4} torr presents the following problems: (i) a large compression ratio must be achieved so that an adequate quantity of material may be presented to the column in a volume that is small enough not to impair the resolution of the separation; (ii) the sample compression and introduction system must have vacuum properties that are good compared with the sample pressure—in practice this means that the sample system must be able to be pumped to 10^{-6} torr with a negligible leak rate when isolated from the pumps; (iii) the absolute sample size will necessarily be small—for instance 250 ml of gas at 10^{-4} torr contains about 10^{15} molecules at room temperature—thus a flame-ionization detector or a unit of comparable sensitivity is essential and, (iv) the level of background impurity peaks must be low compared to the sample size, and in practice this often means that the background peaks must be reduced below the lower limit of the detector, that is, less than about 10^{13} molecules with a flame ionization detector. Restriction (iv) for most purposes eliminates any system in which a grease or oil lubricant is used, since solution from previous samples in the grease or oil presents a contamination level that can only be overcome by complete dismantling and cleaning. Many commercial gas sample introduction devices use gasketed sliding parts, but we have been unable to discover any such unit with vacuum properties that are even remotely satisfactory for the present purpose. Furthermore, many but not all such devices require the use of a lubricant grease for vacuum-sealing.

WILKINSON AND HALL[1] have described an introduction device in which the sample may be pushed through a barrel-and-key tap into a carrier gas stream. This concept has been developed to meet the present requirements using a modified Springham greaseless stopcock as shown in Fig. 1 and in position S in Fig. 2. The model used had a 3 mm bore. The gas to be injected is compressed with a mercury piston against the nose N of the closed tap until the sample pressure is slightly higher than that of the carrier gas which flows through the body of the tap. Upon opening the tap, the gas sample is rapidly injected into the carrier gas stream. The Springham greaseless stopcock is modified to carry two extra side-arms. The mercury piston is connected to the central tube X, while the carrier gas enters the body of the tap by a bottom side-arm Y and leaves by one near the top Z. The extra tube W at the bottom of the tap is to enable mercury which may occasionally spill over from the injection tube to be drawn off. However, in practice, with a properly adjusted injector, such spillage seldom occurs and should be avoided to prevent column contamination.

This injector has been operated with the system shown in Fig. 2. The gas sample is expanded via V_1 into the evacuated compression bulb B, which is of volume about 250 ml. With V_1 closed the mercury piston is raised and tap T_1 then opened and the mercury level in the reference arm M adjusted to a level about 1 mm higher than the top of the injection tube in S. Since the carrier gas pressure is normally about 1 atm above atmospheric, the mercury must be driven from the lower reservoir with a well controlled compressed air bottle and the glassware must be strong enough to stand the extra pressure. Ordinary construction from moderately heavy

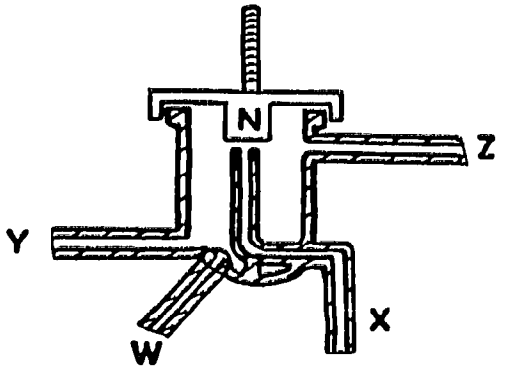

Fig. 1. Sample injector.

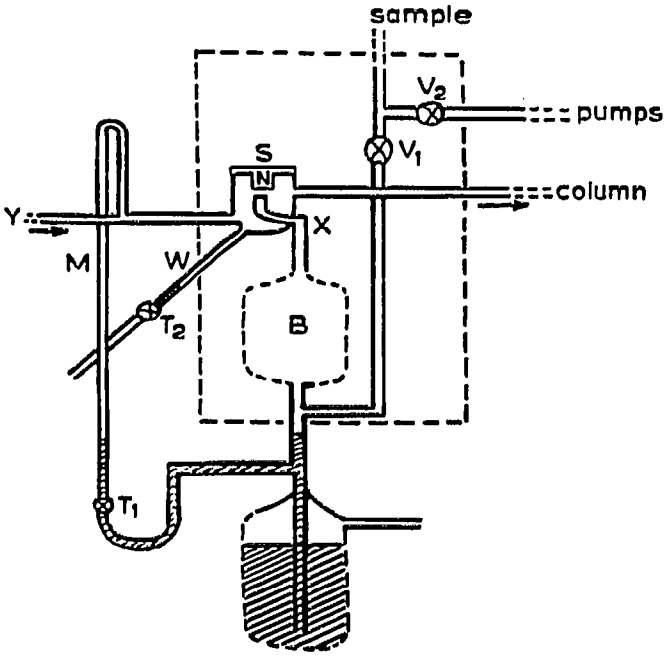

Fig. 2. System for use with sample injector.

walled pyrex is adequate and the greased taps at T_1 and T_2 must be spring-loaded.

Taps V_1 and V_2 are greaseless types such as Veeco Type RSS. Since taps T_1 and T_2 are always covered internally with mercury, they may be made greased types with no risk of gas contamination. Springham greaseless stopcocks are not completely satisfactory in positions V_1 and V_2 because of a tendency to slow leakage between atmosphere and the body of the tap. All of the parts within the dotted line in Fig. 2 are conveniently mounted in a baking oven for outgassing under vacuum, or alternatively they may be heated for this purpose by winding with heating tape.

The injector cannot be used under circumstances where gas compression would lead to condensation of the sample. For non-condensible gases, entirely reproducible results were obtained. Peak height calibrations were reproducible to within 2 % and peak height *vs.* sample size plots were linear over the sample pressure range $5 \cdot 10^{-2}$ to $5 \cdot 10^{-4}$ torr. Typical applications for which this device has been used have included analysis of mixtures of lower hydrocarbons up to C_4.

The equipment has been used for routine research applications over a period of two years with no trouble, and the only maintenance has been the occasional replacement of the Viton A diaphragm in S. For routine use in a non-research environment it may prove convenient to drive the mercury piston by a mechanical piston the travel of which could be controlled by suitably placed stops.

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