The above system has been used for collecting several thousand fractions from a chromatograph with subsequent introduction into a mass spectrometer. It has proven to be efficient and trouble-free.

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## Improved sampling valve for gas chromatography

For the gas chromatographic analysis of engine exhaust and air for trace amounts of hydrocarbons, a gas sampling valve with the following features was required: (1) no detectable gas leaks, (2) no contamination or adsorption of the sample, (3) fast switching speed for instantaneous sample injection, (4) interchangeable sample volumes with the smallest about 0.1 ml, and (5) good sampling precision. Five different valves available for laboratory gas chromatographs have been tried, but all failed to meet these requirements.

KARASEK AND AYERS[1] have described a unique gas sampling valve for use with industrial gas chromatographs. One of these pneumatically operated valves, obtained from the Greenbrier Instrument Company, Ronceverte, West Virginia, is shown in Fig. 1 with a four-way solenoid valve (PAL type, Ross Operating Valve Company, Detroit, Michigan). Either 1/16- or 1/8-in. Swagelok fittings may be used and a 1/16-in. tube delivering a sample volume of 0.14 ml is shown.

As received from the manufacturer the valve leaked seriously, but otherwise showed promise of meeting the above requirements. It therefore appeared worthwhile to develop a method for making the valve gastight. This method and an example of the use of the valve in the analysis of highly diluted hydrocarbon mixtures are discussed in this paper.

The disassembled valve is shown in Fig. 2. The stainless steel part (left) is separated from the brass base by a Teflon diaphragm, which opens and closes the valve ports by means of air pressure. In initial attempts to eliminate leaks, other diaphragm materials were evaluated, including Mylar, polyethylene, polyvinyl chloride, and polyurethane. Only with the last material was the valve gastight at 20 p.s.i.g. nitrogen. However, in trials with nitrogen samples containing 0.1 % benzene, the polyurethane adsorbed 10 times as much benzene as did the Teflon diaphragm, so that it was discarded as unsatisfactory for quantitative work.

The surfaces separated by the diaphragm bore the marks (mainly long scratches) of the grinding operation in the manufacture of the valve. It was found that the valve could be made gastight with Teflon diaphragms by polishing both surfaces to a mirror-like finish. The stainless steel part was first polished with 2/0, 3/0, then 4/0 Carborundum emery paper taped to a glass plate. Finer polishing was done with No. 9, No. 6, and No. 1 diamond pastes (Elgin National Watch Company, Elgin,

Illinois) on Gamal cloth-covered wheels. Linde B alumina, then Burrell C-RO chromic oxide powders on similar wheels were used to obtain a mirror-like finish.

The brass base, being softer than stainless steel, did not require as elaborate a polishing procedure. After removing the alignment prongs, it was polished with Linde A alumina on a wax wheel, then Linde B alumina and Burrell C-RO chromic oxide on cloth-covered wheels.

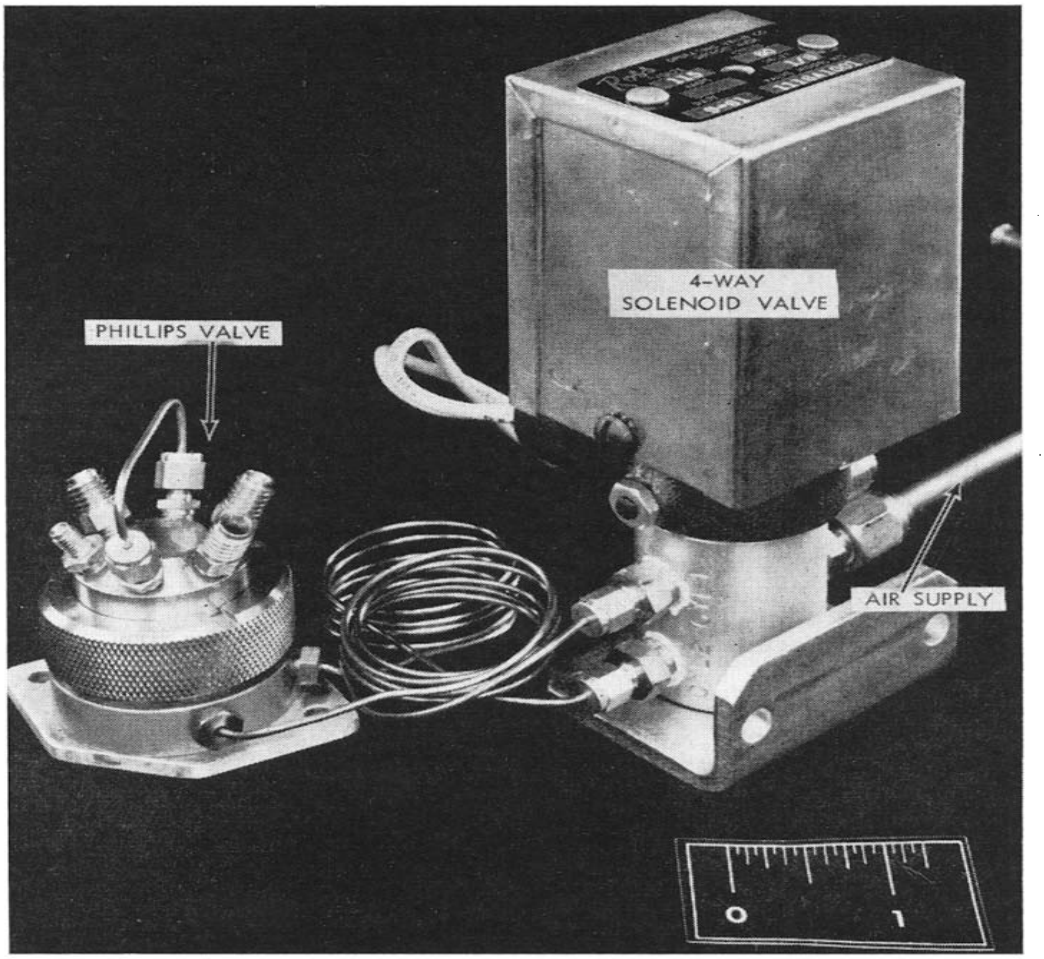


**Fig. 1. Phillips gas sampling valve with air pilot valve.**

The polishing materials that coat the walls of the channels were removed with triple solvent (equal portions of acetone, chloroform and toluene) in an ultrasonic cleaner. The valve was reassembled with a new Teflon diaphragm and tested under water with 70 p.s.i.g. hydrogen (95 p.s.i.g. air pilot pressure). No gas leaks could be detected.

The valve has been routinely used with a laboratory gas chromatograph for about a year, much of the time with 50 p.s.i.g. hydrogen carrier gas. Leaks, particularly at the sample gas ports, have occurred 3 times; but in all cases the trouble was due to minute metal and dirt particles getting into the valve because of inadequate filtering of the gas streams. After cleaning the valve and installing a new Teflon diaphragm, gastight service was again obtained. All streams are now filtered with metal screens and, in some cases, with porous metal discs.

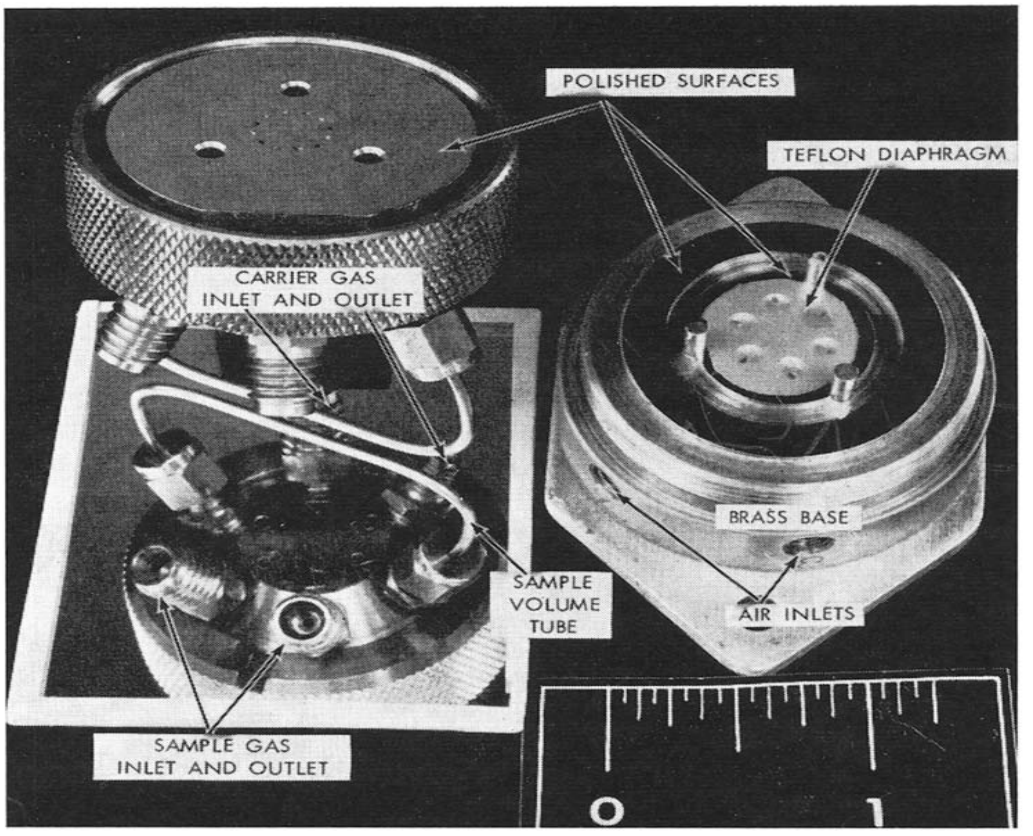


Fig. 2. Disassembled Phillips valve.

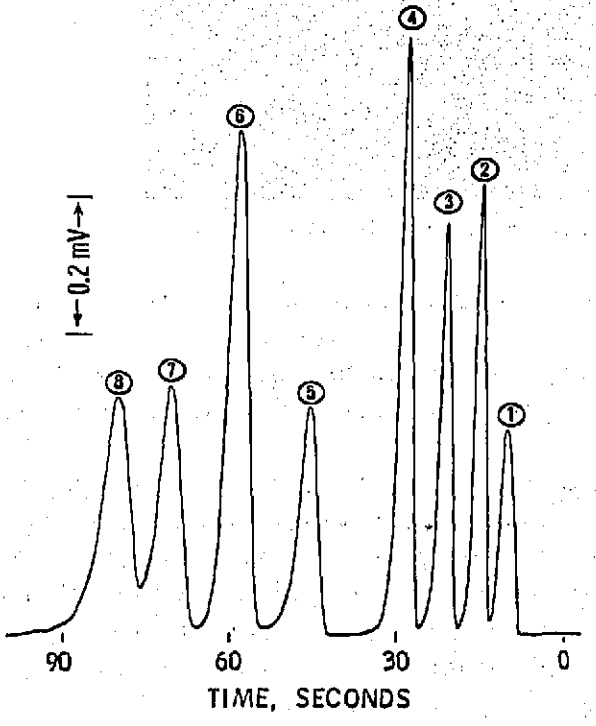


Fig. 3. Chromatogram showing rapid separation using a packed capillary column. Conditions: Perkin-Elmer flame ionization detector, range 1, attenuation × 64. Sample volume: 0.14 ml. Column: 1 m × 0.020 in. i.d. (1/16 in. o.d.) stainless steel tubing packed with 75 mg of 120–140 mesh Burrell silica gel coated with 5 % Apiezon C. Temperature: 26°. Gas flows (23°, 760 mm Hg): 220 ml/min air, 7.4 ml/min $H_2$ carrier gas (50 p.s.i.g. inlet pressure), 65 ml/min 60/40 nitrogen/hydrogen mixture. (1) 215 p.p.m. methane; (2) 195 p.p.m. ethane; (3) 205 p.p.m. ethylene; (4) 215 p.p.m. propane; (5) 195 p.p.m. acetylene; (6) 210 p.p.m. isobutane; (7) 140 p.p.m. *n*-butane; (8) 200 p.p.m. propylene. Balance: nitrogen.

One of the notable features of the valve is the small volume of the internal channels. The volumes of the sample tube shown in Fig. 2 and internal channels are 57 and 83 $\mu$l, respectively, for a total sample volume of 140 $\mu$l. The smallest sample that has been measured with the valve is 86 $\mu$l. By virtue of these small volumes, the valve has been advantageously used with both Golay and packed types of narrow bore columns. Fig. 3 shows an example of the separation of a nitrogen-diluted mixture of eight light hydrocarbons obtained with a 1/16-in. o.d. packed column. The column was connected directly to the valve and stream splitting was neither used nor required. However, stream splitting has been tried and by this means 33 $\mu$l of the same mixture has been separated with an alumina-packed column in one minute.

The precision of the valve has not been extensively investigated; however, the average deviation of peak heights for repeat analyses of dilute hydrocarbon mixtures is usually better than $\pm$ 0.5 %.

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[1] F. W. KARASEK AND B. O. AYERS, *ISA (Instr. Soc. Am.) Journal*, 7, No. 3 (1960) 70.

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