

# GAS SAMPLE INTRODUCTION VALVE

## AN AUTOMATIC SAMPLING DEVICE FOR PLANT ANALYZERS USING GAS CHROMATOGRAPHY

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In order to introduce a gas sample into a gas chromatography column, the sample is commonly trapped in a by-pass tube of a suitable volume. The sample is then pushed into the column by flow of the carrier gas through the tube. This is normally achieved by proper manipulation of the by-pass and main line valves. The sample size depends on the tube volume, the sample pressure and its temperature. A change in the desired sample volume requires a different tube.

The more difficult problem of automatically introducing the gas sample to plant analyzers has been tackled by several methods [1-5] which are basically variations of the by-pass technique. These involve either automation of the commercial Perkin-Elmer 6 port manual sample valve or an automatic manipulation of 2 to 6 valves.

The by-pass system could not be easily adopted to a gas chromatography system, used by the authors in a certain work, carried out at a high pressure where, also, no wastes were tolerated. Moreover, the sample size had to be conveniently changed by remote control. This paper describes a one-valve sampling device, which is suitable for high-pressure as well as for low-pressure systems.

### DESIGN REQUIREMENTS

The reproducibility of the sample size is of great importance in process control. With the sample size and other operating variables, such as temperature, pressure and flow rate constant, the height of the peaks is a function of the composition. This fact can be utilized for control purposes.

A well-designed valve should comply with the following requirements: (1) The pressure of the sample, as well as that of the carrier-gas, must be constant. (2) The temperature of the sample must be constant. (3) The sample must be "plugged" into the column as quickly as possible, with minimum back-mixing. Dragging in the sample results in long tails, thus affecting separation.

The following additional requirements had to be met in the authors' sampling device: (4) The sample valve was to withstand high pressure as

well as a high pressure drop, since the chromatographic column was designed to be operated at high pressure. (5) A fixed sample weight had to be introduced, independent of the pressure of the chromatographic column. (6) No "waste" of sample could be allowed. (7) The gas to be sampled was corrosive. (8) The valve had to be leakproof, both internally and externally.

#### DEVELOPMENT OF THE SAMPLE INTRODUCTION DEVICE

In the system chosen, the sample is introduced to the column by a pressure difference through an electromagnetic valve, i.e. the pressure of the sample is somewhat higher than the pressure of the carrier gas. In order to gain reproducibility of sample size, the degree of the valve opening as well as the duration of opening has to be controlled. Both carrier-gas and sample come from high-pressure cylinders. Standard two-stage pressure reducing valves and fine needle valves are used for low-pressure experimental work. These valves are changed to high-pressure valves for work above 120 psi g. In order to minimize the effect of small pressure fluctuation, the carrier gas is introduced into a 20 l cylinder before entering the system. A drying trap acts very much as a buffer on the sample line. As the valve is operated electrically and the sample is taken directly from the cylinder through a tube, the valve can be installed inside the thermostated apparatus. Both the carrier and the sample flow through a coil of suitable length in the thermostated apparatus before entering the valve. Thus the temperatures of both streams are constant and identical and a temperature gradient is avoided.

Some commercially available solenoid valves were modified and tried out. All developed leakage after a short period of continuous operation. This was probably due to the high pressure drop, the corrosiveness of the sample gas and the continuous "shocks" of the very short energizing cycles. In the usual solenoid valve when the electromagnet is energized the needle is pulled from its seat, usually made of some plastic material, and falls down as the circuit breaks. After some time the seat is deformed and the valve leaks internally. It was desired to have a valve, in which the operating power was delivered in such a way that the needle would leave its seat and return to it as smoothly as possible. Moreover, a metal seat seemed imperative. A "screw" type valve was indicated.

#### DESCRIPTION OF THE SAMPLE INTRODUCTION DEVICE

The sampling device consists of two units, the sample valve and the variable time delay-relay.

*The sample valve.*—The valve (see Figs. 1 and 2) consists of three basic

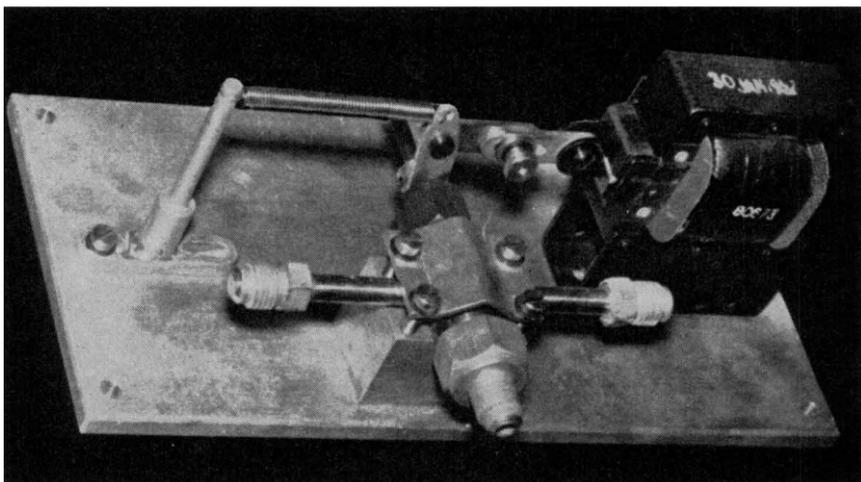


Fig. 1.—Electrically operated sample introduction valve.

elements: (1) a modified high pressure needle valve, made of suitable metal; (2) an electromagnet, with a pull of 500 grams; and (3) a spring.

Once the electromagnet is energized, it pulls a suitable lever (4) thus opening the valve. When the electrical signal breaks, the spring pulls back the lever and the valve is shut. Compared to most solenoid valves, this valve moves smoothly on its thread without jumps and there is no internal leakage. Moreover, by regulating the angle of the lever, the valve opening can be increased or decreased as desired.

In order to “plug” the sample into the column at once without back-mixing, the carrier gas is made to flow continuously through the body of

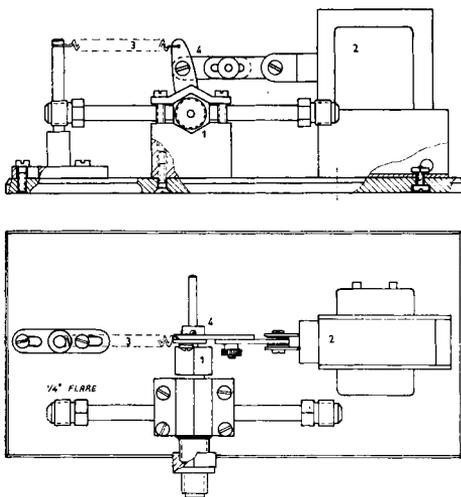


Fig. 2.—Assembly drawing of sample introduction valve.

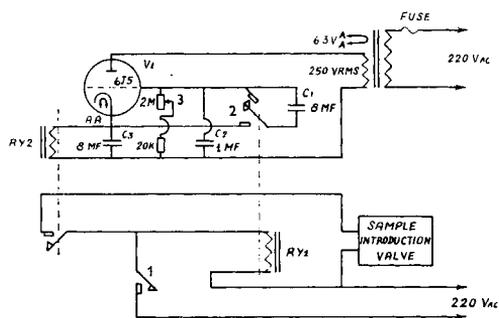


Fig. 3.—Electric circuit of variable time relay.

the valve. This is easily accomplished by drilling an inlet for the carrier gas through the body of the valve and connecting the existing outlet directly to the chromatographic column. The normal inlet of the valve is connected to the sample supply line. A magnetic check valve, not shown in the diagram, is inserted at the carrier gas inlet of the valve. This is a safety precaution, to prevent the ingoing high pressure gas-sample to back into the carrier supply line.

*The variable time delay-relay.*—The signal for sample introduction occurs in our system (to be published at a later date) when the last component of the previous sample leaves the chromatographic column. This is usually unnecessary for most process controllers and plant analyzers. An electric clock, providing an electrical contact at constant time intervals, depending on the elution time of the sample, may be used for most control units.

The variable time delay-relay (Fig. 3) is controlled by a circuit, with an adjustable RC time constant. The circuit components consist of three condensers, a tube, a resistor, a variable resistor and two electrical relays with values indicated on the diagram. Once the signal is delivered (contact (1) is closed), relay RY1 is energized and contact (2) is closed. This allows enough current to pass through the tube V1, thus energizing relay RY2, which in turn actuates the sample valve. Simultaneously, condenser  $C_1$  is being charged and the grid negative bias of the tube increases exponentially. When the potential across  $C_1$  reaches a certain value, RY2 is de-energized, thus de-activating the sample valve. By varying resistance (3), the time of operation of the valve (approx.  $RC_1$ ) can be adjusted from 0.1 to 10 seconds.

## PERFORMANCE

The sampling device has been operating continuously for 6 months. The only maintenance needed was cleaning the relay contacts. The combination of variable pressure drop, the degree of valve opening and the length of time

of valve opening gave excellent control of sample size. It was found that sample size was controllable by changing the pressure drop and time of valve opening only. It was not necessary to manipulate the lever and change the angle of valve opening. Samples of a fixed weight could be introduced, independent of column operating conditions. Samples from 0.02 to 4 millimole were obtained, with excellent reproducibility.

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#### REFERENCES

1. AYERS, B. O., in *Gas Chromatography*, pp. 249-66. COATS, V. J., NOEBLES, H. J. and FAGERSON, I. S. eds. Academic Press, New York, 1958.
2. GREENE, S. A. and CAIN, E. F. C., in *Principles and Practice of Gas Chromatography*. Pescock, R. L. ed. John Wiley & Sons, New York and London, 1959.
3. HELMS, C. C. and SLAUDY, H. N., in *Gas Chromatography*, pp. 267-79. COATS, V. J., NOEBLES, H. J. and FAGERSON, I. S. eds. Academic Press, New York, 1958.
4. HOOIMEJER, J., KWANTS, A. and VAN DE CRAATS, F., in *Gas Chromatography*, pp. 288-99. DEST, D. J. ed. Butterworths, London, 1958.
5. JANAK, J., *Z. Anal. Chem.* **164**, 62 (1958).