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## Note

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### Determination of the volume of the gas sampling valve for chromatographs

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The quantitative gas chromatographic analysis of gas samples often requires the accurate measurement of the size of the sample injected into the chromatographic column. The direct determination of the sampling volume is difficult and in many instances impossible. This problem is usually solved in an indirect way, the commonest techniques being the method of standard additions<sup>1</sup> and the method involving filling the sampling valve with a liquid, with subsequent measurement of the volume or mass of this liquid<sup>2,3</sup>.

The method of standard additions<sup>1</sup> consists in determining the permanent volume of the gas sampling valve and in adding it to the volume of the sampling loop measured by weighing. The permanent volume of the valve is derived graphically from the results of a chromatographic analysis of gas samples of constant composition with several sampling loops replaced consecutively. The method is simple and provides an accuracy of a few per cent. Its principal disadvantage lies in the need for loop replacement, which may result in variations of the sampling volume even when the same loop is used because of differences in its mounting and accommodation in the barrel of the valve.

The second method<sup>2</sup> is based on filling the gas sampling valve with a 1–2 *N* solution of sodium hydroxide, which is subsequently removed by means of distilled water and the amount of the alkali is determined accurately by titration. It has also been proposed to use a volatile liquid as the filler, the displacement being achieved by means of an inert gas until complete evaporation of the liquid, with subsequent measurement of its mass<sup>3</sup>.

The latter two methods do not involve manipulation of the valve–loop system in the course of calibration, but they have the disadvantage of the need for complete removal of air bubbles occluded on the inner surfaces in contact with the gas from the volume to be measured.

These limitations can be eliminated if the valve calibration is performed by measuring the volume of the gas displaced from it\*.

Based on this principle, we have developed a simple and reliable method for the determination of the volume of the gas sampling valve that consists in filling

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\* The possibility of calibrating a gas sampling valve by measuring the mass of carbon dioxide filling the sampling volume has been pointed out before<sup>4</sup>, but no details of the experimental technique used were given.

the valve with nitrogen and its subsequent replacement with carbon dioxide. Small amounts of nitrogen (left after the absorption of carbon dioxide with an alkali) can readily be measured by means of standard equipment and techniques widely used in elemental analysis (nitrogen determination by the Dumas method)<sup>5,6</sup>.

## EXPERIMENTAL

The equipment used is shown schematically in Fig. 1. To carry out a measurement, the inlet sleeve of the gas carrier line of the valve to be calibrated (5) is connected with a supply of carbon dioxide. The outlet sleeve of this line of the valve (6) is attached to a nitrogen microanalyser\*. Note that nitrogen can be displaced from the valve only with carbon dioxide freed completely from impurities that are not absorbed by an alkali (primarily oxygen and nitrogen). Carbon dioxide of the required purity is obtained in a generator (1) by the technique described in detail by Kirsten<sup>6</sup>. Valve (2) serves for smooth control of flow-rate of carbon dioxide.

### Measurement technique

The sampling valve is placed in the "filling" position (the sampling loop is disconnected from the carbon dioxide flow) and the system is purged with carbon dioxide at a rate of 20 ml/min until the gas leaving the valve begins to absorb completely in the nitrogen analyser (as revealed by the formation of bubbles). Next, the valve is filled with pure nitrogen by passing the gas through the sampling loop at a rate of 20 ml/min. The total amount of gas passed should be 5-7 times the expected sampling volume of the valve. About 3-5 sec after the nitrogen flow has been stopped, one makes sure that the pressure in the system has become equal to at-

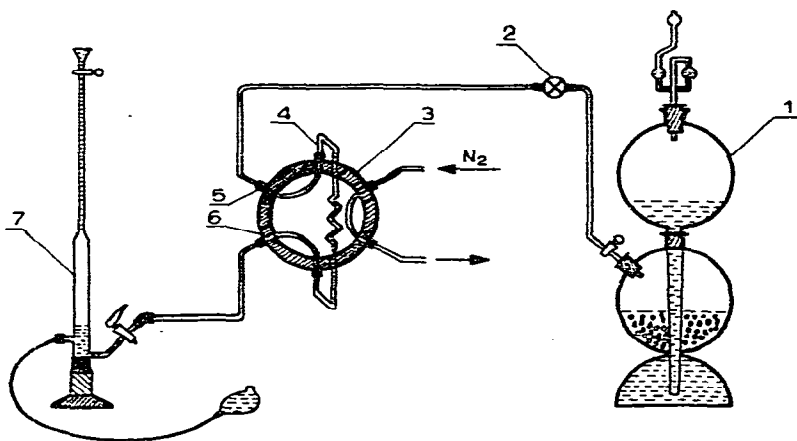


Fig. 1. Equipment for determining the sampling volume of gas valves in chromatographs. 1 = Kipp's apparatus; 2 = fine control valve; 3 = barrel of 6-port gas sampling valve; 4 = replaceable sampling loop; 5 = inlet to carrier gas line; 6 = outlet from carrier gas line; 7 = nitrogen microanalyser.

\* The technique of measurement (see below) does not involve dismantling of the sampling valve in instances where it is already mounted on the gas chromatograph (e.g., in a special thermostat) and permits the valve to be calibrated directly at its operating temperature.

mospheric pressure (as checked by a soap bubble meter), the valve is transferred to "sampling" and the nitrogen is displaced with carbon dioxide into the nitrogen analyser until minute bubbles begin to form in it.

The volume of nitrogen thus collected ( $V_{\text{meas}}$ , ml) is measured every 15–20 min, in accordance with the recommendations<sup>5,6\*</sup>. The time needed for one determination is 30–50 min, depending on the actual loop volume.

The sampling volume ( $V$ , ml) is calculated by eqn. 1, taking account of the temperature of the gas valve ( $t$ , °C), that of the nitrogen microanalyser ( $t'$ , °C), the barometric pressure ( $B$ , mmHg) and the temperature of the mercury pressure gauge ( $t_B$ , °C). In addition, one should introduce corrections for the water vapour pressure above the 50% potassium hydroxide solution at the temperature of the nitrogen analyser ( $w$ , mmHg) and for the adhesion of copper oxide particles in the nitrogen analyser (a factor of 0.98).

$$V = \frac{V_{\text{meas}} \cdot 0.98 \left( B - \frac{t_B}{8} - w \right) (273.2 + t)}{B (273.2 + t')} \quad (1)$$

The gas sampling valve used was a heated six-port valve with four sampling loops with volumes of 0.16, 0.60, 1.18 and 4.21 ml\*\* mounted in a special self-contained thermostat of a Perkin-Elmer 900 chromatograph.

The sampling volumes were determined by the above method at the valve thermostat temperature of 110–115°, controlled by a mercury thermometer to within 0.1°. Standard equipment employed in the Dumas<sup>5,6</sup> nitrogen determination technique was used (see Fig. 1). Carbon dioxide was prepared in a 2-l Kipp's apparatus in accordance with the recommendations<sup>6</sup>.

As the gas of constant composition to be chromatographed we used an air-vapour mixture equilibrated with a saturated aqueous solution of benzene in a special 100-ml hypodermic syringe thermostated at 10<sup>07</sup>.

#### *Chromatographic equipment and conditions*

A Perkin-Elmer 900 chromatograph, equipped with a 2 m × 3 mm I.D. steel column and filled with Dynochrom H (0.25–0.315 mm) was used, with 15% polyethylene glycol adipate, nitrogen as the carrier gas at a flow-rate of 30 ml/min, a column temperature of 70°, an evaporator temperature of 200° and a gas valve thermostat maintained at *ca.* 110°. A flame-ionization detector was used. The peak areas were measured with a Takeda Riken 2213 integrator.

#### RESULTS

The method was used to determine the sampling volumes of a six-port gas valve with four sampling loops. It was checked by means of the method of standard additions<sup>1</sup>, which is essentially based on measuring the mass of water filling the

\* The sampling loop volume of *ca.* 4.5 ml, which exceeds the volume of the nitrogen microanalyser (2.5 ml), was measured in two steps.

\*\* Derived from the mass of distilled water filling the loop.

TABLE I

DETERMINATION OF GAS VALVE SAMPLING VOLUMES BY THE PROPOSED METHOD AND THE METHOD OF STANDARD ADDITIONS

Sampling volume (ml)				Difference, I-II (ml)	I-II I (%)
Method proposed in this work (I)		Method of standard additions (II)			
Individual results	Mean	Individual results	Mean		
0.260	0.265	0.260	0.255	0.010	3.77
0.270		0.250			
0.270		0.260			
0.710	0.715	0.700	0.695	0.020	2.80
0.710		0.690			
0.720		0.700			
1.280	1.275	1.280	1.275	0	0
1.275		1.270			
1.270		1.280			
4.265	4.265	4.290	4.295	0.030	0.70
4.250		4.290			
4.280		4.300			
		4.300			

loop. This method was chosen for reference because, in the absence of a reference gas valve, the proposed method should be based on different principles than the comparison. This reduces to a minimum systematic errors inherent in both methods, which are most difficult to establish.

The results obtained with these two methods are presented in Table I and show that the disagreement does not exceed a few hundredths of a millilitre, which represents *ca.* 4% for the small volume (*ca.* 0.3 ml) considered. For larger samples, the disagreement is less than 1%.

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