

CHROM. 14.908

## Note

### Chromatographic sampling valve for dynamic kinetic experiments

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(Received March 17th, 1982)

The classical method of studying kinetics of heterogeneous catalysis is the measurement of reaction rates under steady-state conditions, *e.g.*, in a continuous stirred flow reactor (CSTR). More information can be obtained in non-steady-state (dynamic) kinetic studies (*e.g.*<sup>1,2</sup>), by effecting a step, pulse, periodic oscillation, etc. in the steady-state value of some parameter influencing the steady-state (usually feed-composition or feed-rate) and observing the response of the catalytic system (most often the composition of the reactor output stream). Since the response can be very rapid, it is necessary to analyse the output stream in short time intervals or continuously. The devices currently employed are usually either expensive or difficult to operate (*e.g.*, mass spectrometer) or single-purpose (continuous spectral analysers). In this work we describe the principle and design of a sampling valve which enables one to employ a gas chromatograph to analyse the reactor output stream even for rapidly changing composition.

A diagram and sectional view of the sampling valve are given in Fig. 1. The valve is formed by two fixed stainless-steel disks 1 and 2 between which a stainless-steel turning disk 3 is placed. Twelve holes 4 (diameter 2.6 mm) are bored in the turning disk, each representing one sampling chamber (volume 0.21 cm<sup>3</sup>). Two holes 5 (diameter 2.6 mm) are bored in each fixed disk. Carrier gas enters one hole in the upper disk 1 and passes through a sampling chamber inside the turning disk 3 to the chromatographic column. The reaction mixture enters the second bore in the upper disk and is vented after passing through the sampling valve. The handle 7 serves for turning the disk 3 round the PTFE sleeve-bearing 6. The closeness of contact of disks is ensured through PTFE annuli 8, which are tightened by screwing in the nut 9 above the spring 10.

When the moving disk is turned clockwise by one hole (chamber) the content of the chamber is sampled directly into the chromatographic column. If it is necessary to take the next sample from the reaction mixture and the analysis of the previous one is still incomplete, it is sufficient to turn the moving disk counter-clockwise by one chamber. By turning in the counter-clockwise direction, it is possible (with twelve chambers) to take and store altogether ten samples regardless of the time required for one chromatographic analysis. The "stored" samples can be analysed later, when the catalytic system approaches a new steady-state and where (because of the monotonous relaxation curves) it is not necessary to analyse so frequently. After analysing the

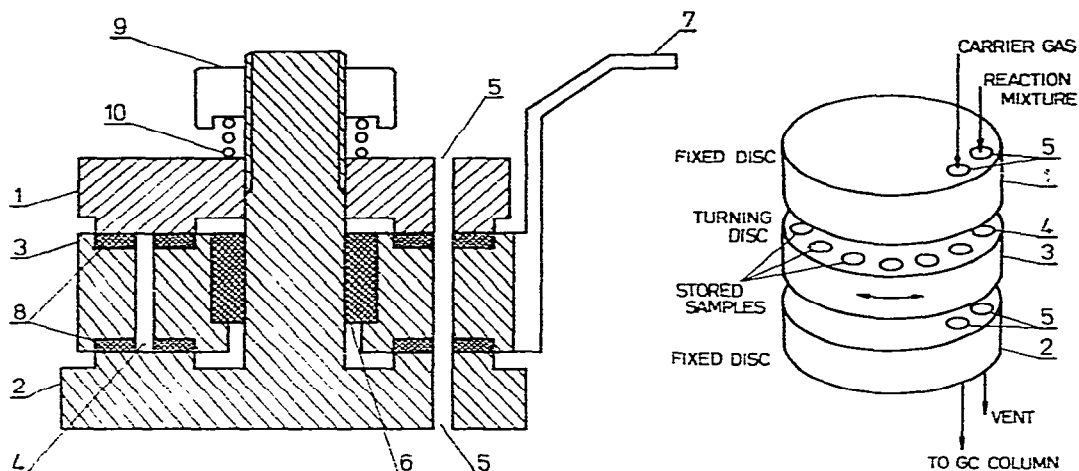


Fig. 1. Sampling valve; for description see text.

"stored" samples, it is possible either to sample directly into the chromatographic column (by clockwise turning of the moving disk) or to store new samples (counterclockwise turning of the moving disk). The best sampling strategy depends on the properties of the catalytic system studied and on the shape of the relaxation curves. By increasing the number of chambers in the moving disk it is possible to increase the "storage capacity" of the sampling valve.

The tightness of the sampling valve was checked experimentally. Ten sampling chambers were filled with an equimolar gas mixture of dimethyl ether and nitrogen. These samples were analysed by chromatography and it was found that the composition in the sampling chambers did not change practically for 30 min (Table I). After storage for 60 min, about 10% loss of the dimethyl ether and nitrogen was observed, as evidenced by a decrease in peak areas. At the same time the mole fractions determined from the peak areas changed only slightly (Table I).

Use of the chromatographic sampling valve in a dynamic study of methanol dehydration on an ion exchanger catalyst<sup>3</sup> is illustrated in Fig. 2, where the CSTR response to a step change in feed composition (from pure nitrogen to 20 mol %,

TABLE I  
TIGHTNESS OF SAMPLING VALVE

DME = Dimethyl ether.

Sample storage time (min)	0	5	15	30	60
<i>Peak area*</i>					
N <sub>2</sub>	29,940	29,900	29,020	28,100	27,050
DME	34,020	33,840	33,480	32,820	29,600
<i>Mole fraction</i>					
N <sub>2</sub>	0.50	0.50	0.50	0.49	0.51
DME	0.50	0.50	0.50	0.51	0.49

\* Arbitrary units.

nitrogen– 80 mol % methanol) is shown. The reaction mixture was separated at 180°C on a 50-cm column (2 mm I.D.) with equal amounts of Sphero carb (80–100 mesh) and Porapak P (80–100 mesh). Hydrogen (20 cm<sup>3</sup>/min) was used as the carrier gas; the detector was of the thermal conductivity type. The time for one analysis was approximately 2.5 min. During the first 10 min, when the composition of the reaction mixture changes quickly, samples were taken in 1-min intervals and stored; they were analysed after the system had approached the steady-state.

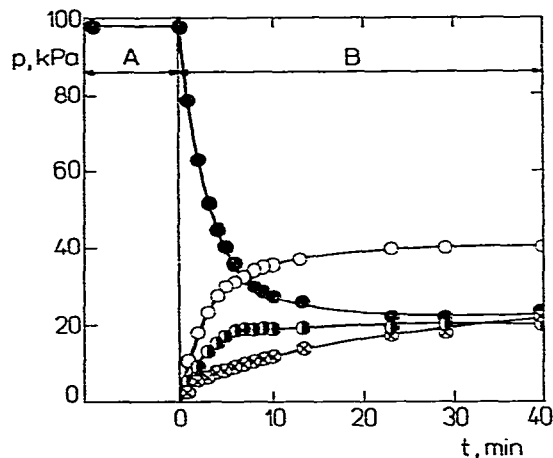


Fig. 2. Time profile of partial pressure of the reaction mixture components,  $p_i$ , in the CSTR after a step change in feed composition; A = pure nitrogen, B = 20 mol % nitrogen–80 mol % methanol. (○, Methanol; ◐, dimethyl ether; ⊗, water; ●, nitrogen).

The sampling valve described should be especially useful for the experimental study of catalytic systems having relaxation curves with sharp extremes<sup>2</sup>.

#### REFERENCES

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