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Note

A dual-channel micro-reactor for reaction gas chromatography

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In reaction gas chromatography, the sample is reacted with or over certain material (reactant) placed in the flow circuit of a gas chromatograph. The reactant is generally placed either in the injection port of the gas chromatograph, in a column between the injection port and the analysing column, or in a pre-column micro-reactor before the injection port^{1,2}. The last mode mostly employs a tubular micro-reactor provided with an injection port and a gas inlet at the top. In order to obtain a chromatogram of the sample after the reaction, the sample is injected into the micro-reactor through its injection port. It is also frequently necessary to obtain the chromatogram of the sample as such, without reaction, under identical operating conditions for comparison and for deriving differential results. For this purpose, a common procedure is to incorporate some system that allows the introduction of the sample at a point between the micro-reactor and the analysing column^{3,4}.

The above procedure suffers from the serious disadvantage that the retention times of the substances that appear on both of the chromatograms (one after the sample has been injected through the reactor and the second when the sample is injected to by-pass the reactor) usually differ and the difference is proportional to the ratio of the length of the reactor tube to that of the analysing column; also, peak broadening occurs to a greater extent in the first case. This effect was marked in the present author's studies on a subtractive GC system and it made qualitative identifications impossible. Hence conclusions based on a comparison of two chromatograms as described above are difficult to draw.

In order to overcome this disadvantage, *i.e.*, to produce comparable chromatograms corresponding to post-reaction and unreacted component patterns of the sample under the same operating conditions, a modified micro-reactor incorporating a dual-channel system was developed⁵ and was used successfully for subtractive and hydrogenation reaction GC with some hydrocarbon mixtures. This paper briefly describes the design of such a reactor and considers some of its applications.

DESCRIPTION OF THE MICRO-REACTOR

The construction of a typical dual-channel micro-reactor is illustrated in Fig. 1. The reactor consists of dual parallel channels, each provided with a sample

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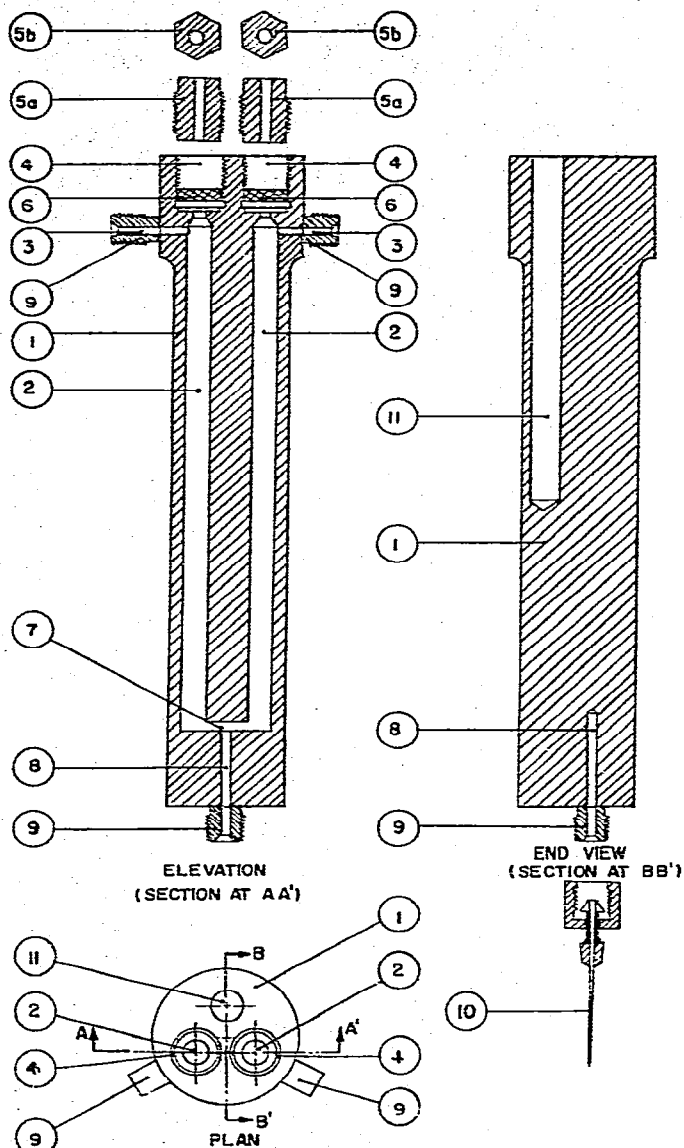


Fig. 1. Construction of the dual-channel micro-reactor for reaction GC. 1 = Reactor body (metallic); 2 = reactor channels; 3 = gas inlets; 4 = injection port (female part, threaded in side); 5a = injection port plug (male part, threaded corresponding to part 4) bearing a central hole to permit injection of samples; 5b = plan view of the head of the injection port plug, suitable for tightening with a spanner; 6 = self-sealing rubber septum; 7 = connecting capillary; 8 = reactor exit (capillary); 9 = Swagelok male fitting; 10 = injection needle with Swagelok female fittings (to be coupled with part 9 at the reactor exit); 11 = thermometer well.

injection port and an inlet for gas at the top. The channels are connected together at the outlet end through a capillary (which may be drilled from outside and then the unwanted portion plugged). The latter is joined at its centre to a capillary exit, which is to be coupled with the analysing column of a gas chromatograph, either directly

through standard fittings or by first coupling the exit end with an injection needle-type accessory and then inserting the needle into the injection port of the gas chromatograph. The whole reactor body is surrounded by a tubular furnace for work at elevated temperatures.

In our work, the reactor was made of stainless steel and had the overall dimensions 17×3 cm O.D., but the material and dimensions could be varied as required.

The reactor has to be packed carefully so as to leave no gaps or dead volume. A glass-wool plug may be placed, from below, at the exit end (8). Some powdered inert material (*e.g.*, 60–80 mesh Chromosorb W) is inserted in the connecting tube (7) and the exit capillary (8) through the upper end (4). It is preferable to insert some Chromosorb W in the reaction channels (2) also (*e.g.*, 30–50% of the lower length)⁶. Some glass-wool can then be placed over the inert support packing. The catalyst, coated over a powdered porous support, is packed in one of the channels (reactant channel) and the support material in the other channel (reference channel). The reaction material can be filled to the desired height, the remaining portion of the channel being filled with the support and glass-wool. The gas inlets are also plugged with glass-wool. Rubber septums (6) are then seated in the injection ports (4) and the plugs (5) are screwed up.

In some instances the reactant channel may contain a size-graded porous reaction material itself (*e.g.*, molecular sieves). The reference channel could then be filled with some identically size-graded inert porous material that gives nearly the same resistance to gas flow.

OPERATION

The same gas is made to pass through the gas inlets and through each reactor tube at the same flow-rate. One arrangement of the flow circuit could be as shown in Fig. 2, as was used in our work where it was found not to be necessary to regulate separately the flow-rate of gas in each channel. However, if necessary, separate valves for flow control can be provided before each gas inlet.

The gas flow is turned on and the unit is heated to the desired temperature. The

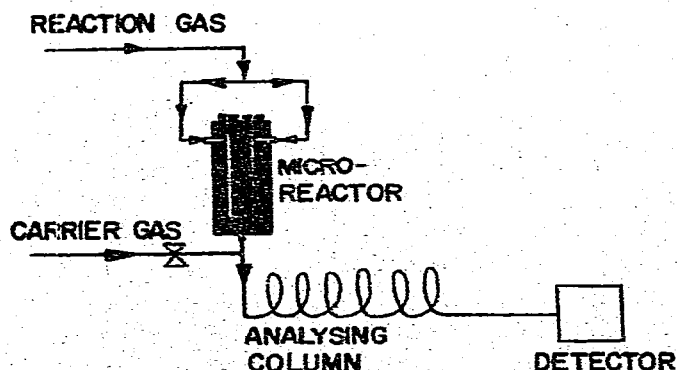


Fig. 2. Flow circuit using the dual-channel micro-reactor as a pre-column.

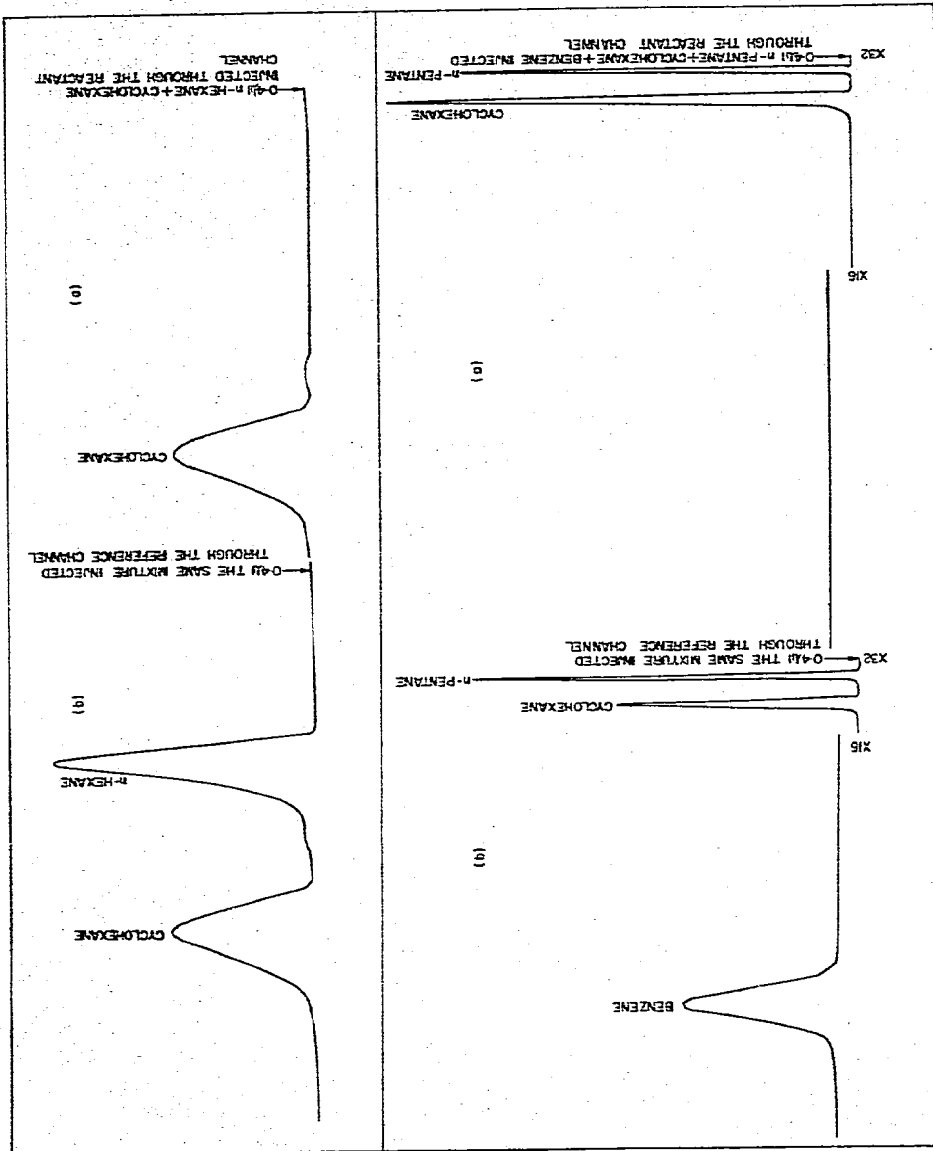


Fig. 3. Typical example illustrating the use of the dual-channel micro-reactor in subtractive GC. Reactant channel, molecular sieve 5A, 60-80 mesh; reference channel, Chromosorb P, 60-80 mesh; reactor temperature, 210°; analyzing column, 40% β,β' -oxydipropionitrile, 1.25 m \times 3/16 in. at 30°.

Fig. 4. Typical example illustrating the use of the dual-channel micro-reactor in a hydrogenation reaction. Reactant channel, 20% reduced nickel catalyst on Chromosorb P, 50-60 mesh; reference channel, Chromosorb P, 50-60 mesh; reactor temperature, 190°; analyzing column as in Fig. 3.

sample is injected into the reactant channel and the chromatogram is recorded. The chromatogram shows the post-reaction component pattern of the sample. The sample is then injected into the other channel and again the chromatogram is recorded. This gives the original component pattern of the sample. The two chromatograms, obtained under similar operating conditions, are then examined in order to obtain a differential comparison.

APPLICATION

Fig. 3 presents a typical example of subtractive GC using the micro-reactor. Molecular sieve 5A, 60–80 mesh, was placed in the reactant channel and Chromosorb P, 60–80 mesh, in the reference channel. On injecting a mixture of *n*-hexane and cyclohexane into each of the channels, chromatograms a and b were obtained. It was found that only *n*-hexane is subtracted by molecular sieve 5A, and that the peak of cyclohexane is almost identical in shape, size and retention time in both instances. Hence the two chromatograms could be superimposed in order to establish both the subtracted and unaffected components.

Another example of a catalytic reaction is shown in Fig. 4. A 20% reduced nickel catalyst, coated over 50–60 mesh Chromosorb P, was placed in the reactant channel, while the reference channel contained 50–60 mesh Chromosorb P. Keeping the reactor temperature at 190°, a synthetic blend of *n*-pentane, cyclohexane and benzene was injected separately into the two channels and chromatograms a and b were recorded, respectively. The two chromatograms are comparable and indicate that only benzene undergoes transformation to cyclohexane without any side-products being formed.

The dual-channel micro-reactor thus facilitates easy interpretations of the results of reaction GC. As indicated in the above examples, the device works satisfactorily for hydrocarbon samples. However, the author has not experimented with polar samples where catalyst surface adsorption may also occur, but support surface effects and path-length differences would be largely eliminated by using the micro-reactor.

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