also true for glycine and proline. Nevertheless, even these amino acids could be separated sufficiently by allowing the solvent to run long enough for leucine to travel about 10.5 inches from the base line in each direction.

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Simplified analysis of light gas mixtures with gas chromatography

The analysis of light gas mixtures including hydrogen, oxygen, nitrogen, methane, carbon monoxide and carbon dioxide is a common problem in gas chromatography. The difficulty in this simple analysis is that only a molecular sieve column can separate oxygen and nitrogen, but at the same time, this column, under normal operating conditions, irreversibly adsorbs carbon dioxide; on the other hand, a silica gel column which is adequate for the other part of the given mixture, does not separate oxygen and nitrogen.

In practice, multiple analysis or column combinations are used to solve this problem. In multiple analysis, two separate runs are made, one on a silica gel and the other on a molecular sieve column; in such cases, either two instruments must be used or the respective column must be changed after the first run.

To overcome the difficulty of the series operation, a special solution was suggested[1] three years ago, where one thermistor bead was installed between the two columns (the silica gel being the first) and another bead after the molecular sieve column. Thus, the carbon dioxide peak is also recorded before it is adsorbed on the second column. Of course, the disadvantage of this system is that carbon dioxide contaminates the molecular sieve, reducing its life. Similar systems were also described in more recent publications[2].

Another possibility for column combination is the use of the two columns in parallel[3]. However, even in this case, the molecular sieve will become slowly contaminated by CO_2. Another disadvantage of this method is that a proper and constant flow splitting is essential to the success of the method.

In this communication we suggest additional solutions, each of which can be carried out very conveniently.

In the first case, a special four-valve system[4,5] is attached to a commercial gas chromatograph (Figs. 1 and 2); this system allows the installation of three different

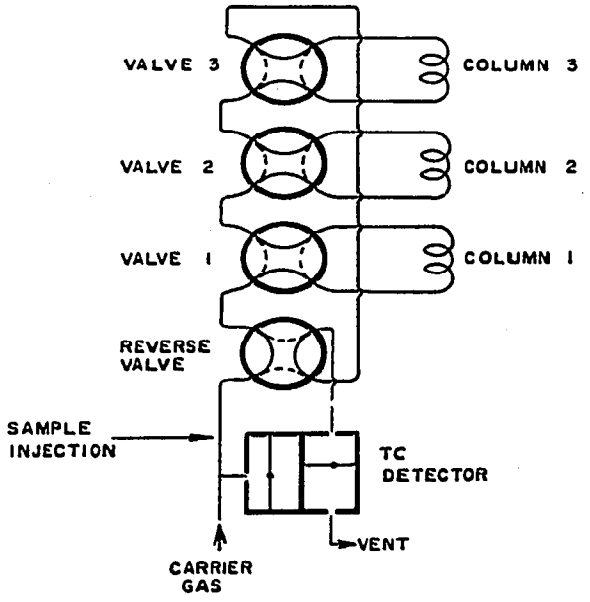

Fig. 1. Schematic of the valving system.

coiled columns along with a reverse flow valve; the valves in the device are of the four-port type using a Teflon rotor[6]. The carrier gas flows past the reference side of the thermal conductivity detector and the sampling system, and into the reverse flow valve. The carrier and sample then flow into the three columns in series, or any combination of these three columns and again into the reverse flow valve. By turning the individual valves, each column can be disconnected from the gas flow during analysis, or all the columns still in the carrier gas flow can be backflushed by turning the backflush valve.

With this system, the light gas analysis can be solved in two ways. The first possibility is to install two columns in the system and inject two consecutive samples into the instrument. During the first analysis, the two columns are in series and therefore all components, except carbon dioxide (which will be adsorbed on the molecular sieve column) will be detected. For the second analysis, the molecular sieve column is disconnected; thus, CO_2 can be separated very quickly from the other components which will give one peak on the second run.

Figs. 3A and B demonstrate this application. The first column was 50 cm long and packed with molecular sieve 5A; the second column consisted of 18 wt.-% hexamethyl phosphoramide on Chromosorb P 60/80 mesh and was 6 m long. The outside diameter of the columns was 1/4 in. and the system was operated at room temperature. The total analysis time can be reduced working at higher temperatures (50–75°), or using higher flow rates.

The advantage of this system is that the two columns can remain installed in the gas chromatograph and thus, no time is necessary for column change. The only dis-

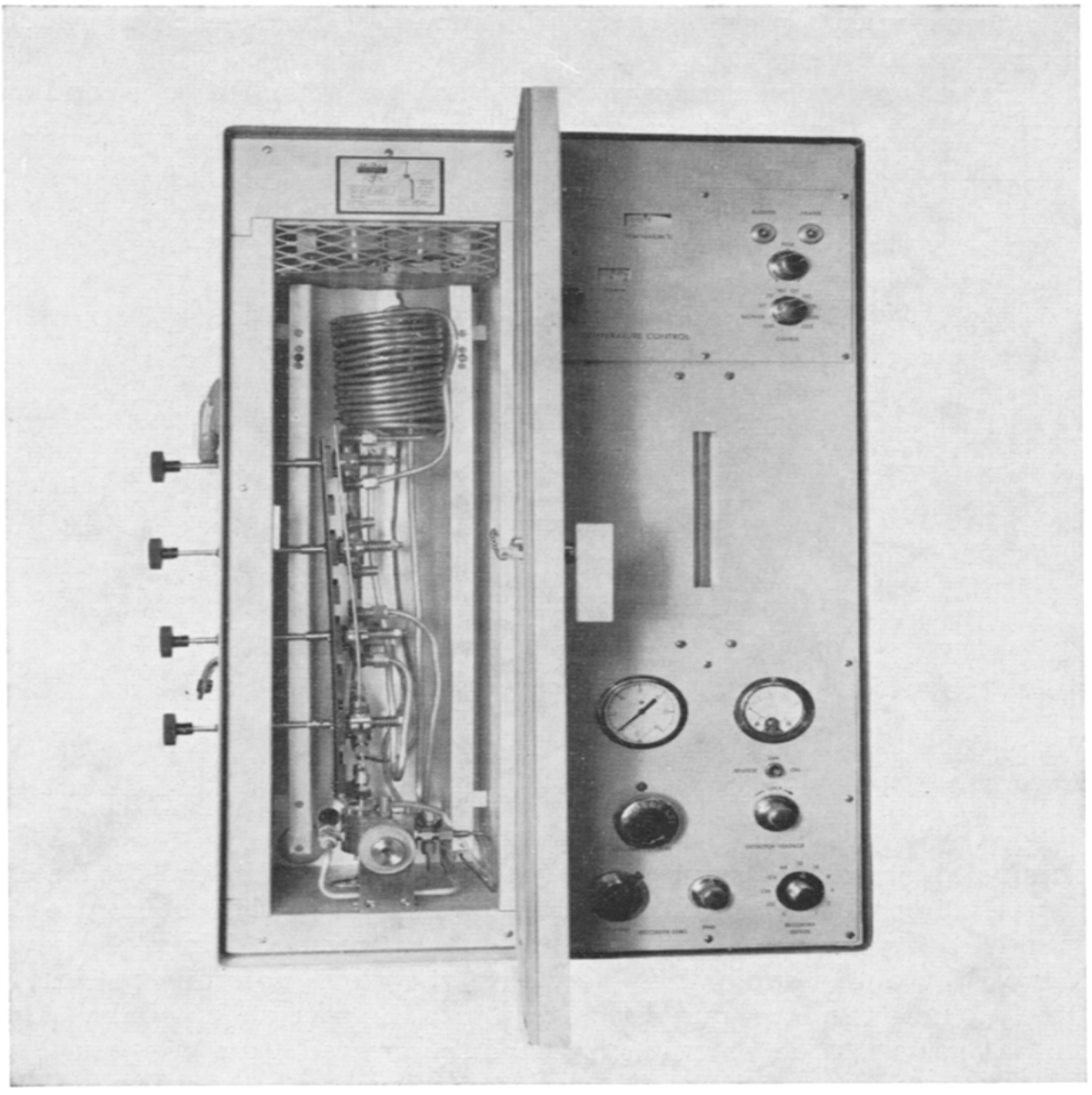

Fig. 2. Valving system and column installed into a Perkin-Elmer Model 154-D gas chromatograph.

advantage of this method is that the molecular sieve will still be contaminated with CO_2. However, if appropriate lengths for the individual columns are selected, it is also possible to analyze this particular sample in one run. In this case, the molecular sieve column would be connected to valve No. 3 and the analysis would start with the carrier gas flowing first to the columns in series. The molecular sieve column would be disconnected before the CO_2 fraction enters it. Thus, the CO_2 fraction would reach the detector directly and be the first peak. Then, by turning valve No. 3, the molecular sieve column would again be connected to the carrier gas line, and the first five components (H_2, O_2, N_2, CH_4 and CO) could be separated on this column. If a silica gel column is substituted for the hexamethyl phosphoramide column, the lengths of the two columns can be selected so that the CO_2 fraction would still be in the silica gel column, while the other components are separated on the sieve column. Thus, this column could be disconnected after the carbon monoxide peak reached the detector; in this way, the CO_2 peak would be the last.

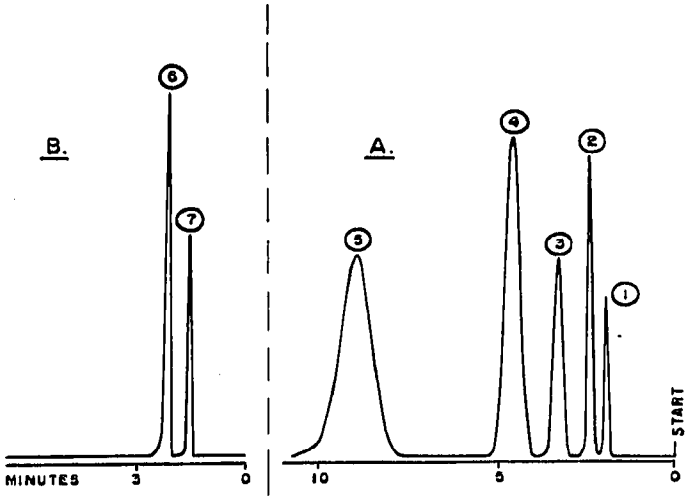

Fig. 3. Chromatograms of a light gas mixture analyzed on (A) 50 cm molecular sieve 5A and (B) 6 m hexamethyl phosphoramide columns. Room temperature. Carrier gas (helium) inlet pressure: 14 p.s.i.g. Thermistor detector. Peaks: (1) hydrogen; (2) oxygen; (3) nitrogen; (4) methane; (5) carbon monoxide; (6) carbon dioxide; (7) $H_2 + O_2 + N_2 + CH_4 + CO$.

Another advantage of the described system is that it also conveniently allows protection against water adsorption on the adsorption columns. It is known that most of the light gas samples analyzed in practice are wet. During conventional analytical methods, the water will be adsorbed (together with CO_2) on the molecular sieve column reducing its lifetime significantly. However, using a combination where the molecular sieve and the silica gel or hexamethyl phosphoramide column are connected to valves 3 and 2 respectively, a third column which has a long retention time for water and a short time for the light gases (*e.g.*, polyethylene glycol on Teflon powder) can be connected to the first valve. Immediately after the light gases pass this column, it should be disconnected, thus preventing water from entering into the other columns. After the whole analysis is completed, this auxiliary column can be backflushed.

The valving systems described can also be used for many other purposes where column combinations or backflushing are necessary.

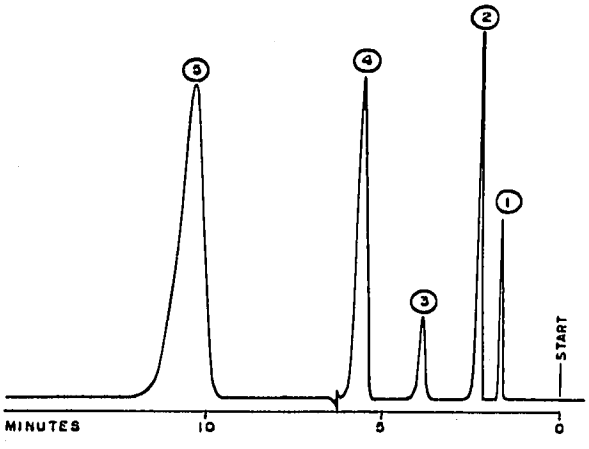

Fig. 4. Chromatogram of a light gas mixture analyzed on a column with dual packing using a backflushing valve. Temperature: 50°. Carrier gas (helium) inlet pressure: 14 p.s.i.g. Thermistor detector. Peaks: (1) oxygen; (2) nitrogen; (3) methane; (4) carbon monoxide; (5) carbon dioxide.

The second possibility is to use backflushing for the CO_2 analysis. With a 2 m silica gel and a 2 m molecular sieve 5A column installed in series in the valving system, the analysis can be carried out in the following way: first, the carrier gas (and sample) is flowing through the system in the given order. The retention time of carbon dioxide in the silica gel column is long enough to allow the separation of the first four components (O_2, N_2, CH_4 and CO) while the CO_2 fraction is still in the silica gel column. After the carbon monoxide peak reaches the detector, the flow through the system has to be reversed; thus, the CO_2 peak will be eluted directly from the silica gel column without being adsorbed on the molecular sieve column.

This mode of operation can be simplified even more. One can pack one single column with the two column materials. Fig. 4 illustrates this modification. Here a 4 m long, 1/4 in. O.D. column is used; the first half of it is filled with silica gel while the second contains the molecular sieve 5A, and the column is connected through a single backflushing valve with the detector. The CO_2 is backflushed from the silica gel portion of the column after the CO peak is eluted from the molecular sieve.

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