

MOLECULAR SIEVES AS SUBTRACTORS IN
GAS CHROMATOGRAPHIC ANALYSISIII. THE SECONDARY EFFECT OF THE MOLECULAR SIEVE
TRAP COLUMN

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(Received May 19th, 1959)

A previous publication¹ dealt with the selective irreversible adsorptivity of the molecular sieves with respect to various homologous series of organic compounds. For illustration of the removal of an adsorbable component, whose peak overlaps partly or completely that of another component, the fractograms of a mixture containing isopropyl ether, propionaldehyde, acetone, ethyl acetate and ethanol were given, analyzed on a standard partition column alone and with a short molecular sieve 5 Å column in series. The fractogram showed that the propionaldehyde peak (and the peak of ethanol) was completely removed.

One purpose of the investigations was to show the analysis of a small amount of acetone in propionaldehyde, since in a normal partition system these components overlapped almost completely. Upon injection into a series column system of molecular sieve and partition column, the unexpected result was found to be that neither component was eluted. This result was confirmed by many repetitions.

This observation induced us to investigate this phenomenon in detail.

EXPERIMENTAL

The experiments were carried out with a Perkin-Elmer Model 154-C Vapor Fractometer. A 50 cm long, ¼ in. diameter column was packed with 20–60 mesh "Molecular Sieve 5 Å" and placed in series with a 2 m long standard partition column containing 30 weight-% polyethylene glycol (Carbowax 1500) on Chromosorb 30–60 mesh*. Fig. 1 in our recent publication¹ showed the schema of the instrument.

RESULTS AND DISCUSSION

We prepared propionaldehyde–acetone mixtures with different acetone concentrations and analyzed them under the given conditions with the gas chromatograph. At higher

* The column designations of the Perkin-Elmer Corporation are the following: molecular sieve 5Å column: column I; polyethylene glycol column: column K.

acetone concentrations we regularly obtained, as expected, the acetone peak, and the propionaldehyde was adsorbed completely on the trap column. It was found, however, that low concentrations of acetone in propionaldehyde would give no peak at all: only levels above 5 % produced any peak response. However, by changing the matrix material from propionaldehyde to ethyl acetate, full response to 4.8 % acetone concentration was restored.

Fig. 1 illustrates the phenomena mentioned above. Runs A and B show the results of two parallel analyses, running a mixture of 4.8 % acetone in propionaldehyde.

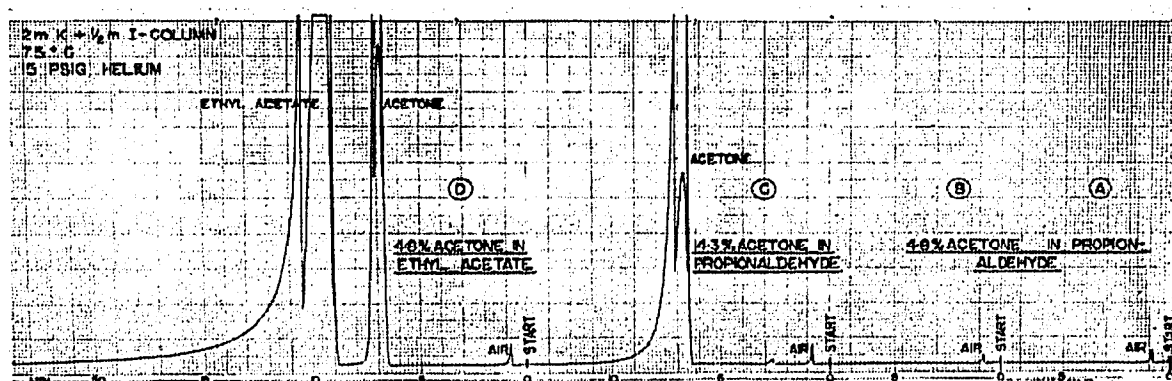


Fig. 1. 2 m K + $\frac{1}{2}$ m I column, 75°, 15 p.s.i.g. helium inlet pressure. The samples: A and B, 4.8 % acetone in propionaldehyde; C, 14.3 % acetone in propionaldehyde; D, 4.8 % acetone in ethyl acetate.

As shown, the analysis would give no peak at all. On the other hand, 4.8 % acetone in ethyl acetate gives an excellent response (run D). Run C shows the analysis of a mixture of 14.3 % acetone in propionaldehyde.

These results suggested that somehow in the presence of propionaldehyde the acetone reacted to form an adsorbable product. In this case, however, on analyzing mixtures with higher acetone concentrations, a certain amount of acetone would subtract from the apparent amount present in each mixture.

For investigation of the value of this supposition, two mixtures were prepared, one of 10 % acetone in propionaldehyde, the other 10 % acetone in ethyl acetate, and analyzed successively through the system. Fig. 2 shows the fractogram of the two analyses. As shown, the response to 10 % acetone is almost exactly twice as great—as seen from the sensitivity notations—for acetone in ethyl acetate as it is for acetone in propionaldehyde. This indicates that about 5 % of the acetone in the propionaldehyde does not elute, which confirms the earlier “threshold” finding.

This secondary adsorption effect was observed in other cases too, *e.g.* in the case of water solutions, which is illustrated with another examination.

The analysis of organic solvents dissolved in water is a general problem and in earlier work² gas chromatography was used for the analysis of very small amounts of isopropyl ether (below 0.5 %) in water. This method, however, has two difficulties: because of the large amount of water, the sample must be analyzed at 100° and even at this temperature, the water peak shows severe tailing. Therefore, the analysis takes

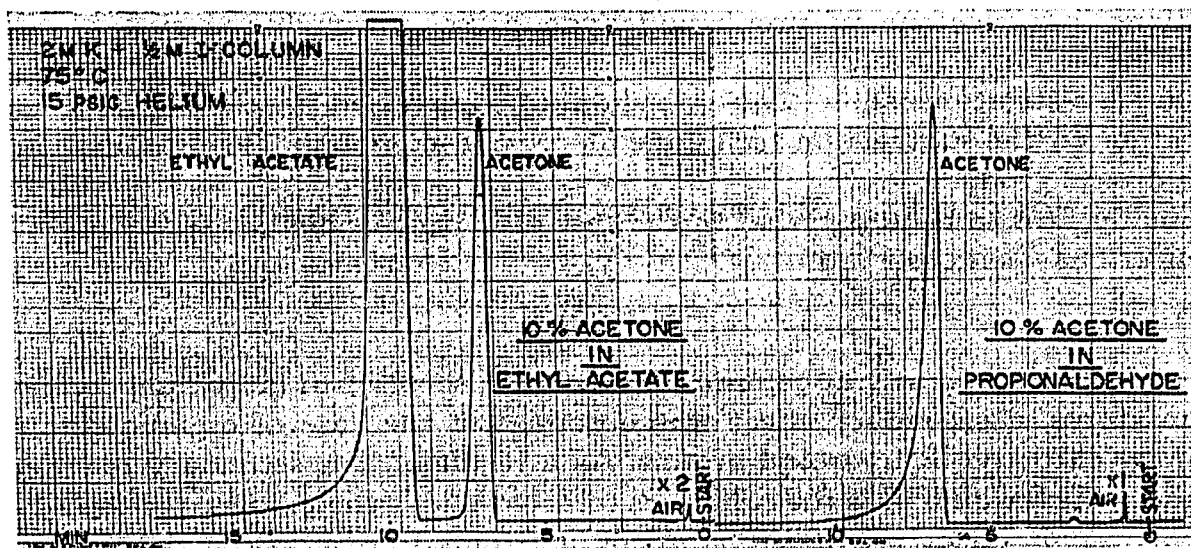
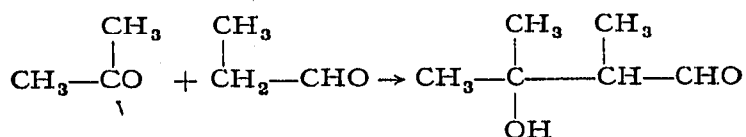


Fig. 2. 2 m K + $\frac{1}{2}$ m I column, 75°, 15 p.s.i.g. helium inlet pressure. Sample at the right analysis: 10 % acetone in propionaldehyde; at the left analysis: 10 % acetone in ethyl acetate.

a long time. We tried to carry out the analysis using a trap column containing molecular sieve 5 Å, with the supposition that in this case the water would be adsorbed on this column. Actually the water peak disappeared but—similar to the analysis of acetone in propionaldehyde—no peak was obtained for the isopropyl ether either.

For the interpretation of the phenomena described above, we suppose the following:

(a) Because the molecular sieves are basic substances, the passage of acetone-propionaldehyde mixtures over this material would tend to create suitable conditions for an aldol condensation reaction. Since the resulting product would be an aldehyde



it would be adsorbed on the sieve. The concentration of 5 % acetone and 95 % propionaldehyde would correspond to the equilibrium on the given conditions.

(b) In the case of the isopropyl ether-water mixture, secondary hydrogen bonding between the adsorbed water and the ether cause the retention of the ether on the column.

The equilibrium conditions of the aldol condensation on the column are dependent on several parameters, *viz.* the temperature, the concentration of the acetone in the propionaldehyde, etc. The effect of the temperature is double: on raising the temperature the conditions become more favorable, but at the same time, the retention time of acetone is shorter on the molecular sieve column and according to this, the contact time is shorter, which results in a lower yield of the condensation product. Thus, our examinations show that at 100° temperature but otherwise under the same

conditions, 5 % acetone in propionaldehyde passes through the system and the equilibrium is much lower.

Our investigations show that care should be exercised in selecting problems for application to the subtraction technique of organic compounds containing carbonyl and hydroxyl groups.

Finally, it is to be noted, that in the case of hydrocarbons³ no secondary adsorption effect has been observed.

SUMMARY

Using molecular sieves as trap column for specific adsorption of individual components from mixtures, a secondary effect was observed in the case of organic compounds containing carbonyl or hydroxyl groups. As a result of this secondary reaction, the substance which would pass the column is retarded under the influence of the adsorbed component. This effect might probably be attributed to an aldol condensation or formation of secondary hydrogen bonds. These reactions could promote the basic character of the molecular sieves. In the case of hydrocarbons, no secondary adsorption effect has been noted.

REFERENCES

¹ N. BRENNER, E. CIEPLINSKI, L. S. ETTRE AND V. J. COATES, *J. Chromatog.*, **3** (1960) 230.

² L. S. ETTRE, unpublished result.

³ N. BRENNER AND V. J. COATES, *Nature*, **181** (1958) 1401.

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