MOLECULAR SIEVES AS SUBTRACTORS IN GAS CHROMATOGRAPHIC ANALYSIS

II. SELECTIVE ADSORPTIVITY WITH RESPECT TO DIFFERENT HOMOLOGOUS SERIES

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The use of synthetic zeolites of the "molecular sieve" (Linde Air Products Company, Division of Union Carbide and Carbon Corp.) type[1] as column packing material for gas chromatography is well recognized[2–6]. The unique ability of the 5 Å and 13 X types for the separation of oxygen and nitrogen, as well as other light gases, has brought them into widespread use. Molecular sieves, however, also have another useful property for gas chromatography.

In a previous publication[7], selective retention of molecular sieves type 5 Å of *n*-paraffins in mixtures of *n*-paraffins, isoparaffins, cycloparaffins and aromatics was described. This selective retention of *n*-paraffins has been used to aid in qualitative identification of components in complex hydrocarbon mixtures[8].

It was noted in one publication[7] that molecular sieves also show similar selective irreversible adsorptivity with respect to other homologous series. The object of the present work was to determine, which compounds and homologous series are irreversibly adsorbed on the sieve column and which are passed and furthermore, the temperature limitations of the system.

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 "Molecular Sieve 13 X" respectively and installed into the chromatograph. The temperature of operation was 100°. Helium was used as carrier gas and a 2 lb/in.^{2} pressure was sufficient to maintain a 60 cm^3/min flow.

Successive samples of about 2 μl of each compound to be tested were run through the system and the eluted peaks recorded on a 5 mV potentiometer recorder. The components were of high purity ACS, Phillips Research Grade or equivalent.

The samples were selected wherever possible to include the lightest member of a homologous series, the next heavier member and at least one relatively heavy representative member.

RESULTS AND DISCUSSION

The compilation of the investigations on the column filled with molecular sieve 5 Å is given in Tables I and II: Table I gives the materials which pass through molecular sieve 5 Å without adsorptive loss and Table II shows the materials which were found to be completely adsorbed under the described conditions.

TABLE I

COMPONENTS PASSED THROUGH MOLECULAR SIEVE 5 Å COLUMN

Group	*Components tested*
Isoparaffins	Isobutane, Isopentane, 2,3-Dimethylbutane
Aromatic hydrocarbons	Benzene, Toluene, *m*-Xylene
Cycloparaffins	Cyclopentane, Cyclohexane
Iso-olefins	Isobutylene, 2-Methylbutadiene-1,3
Esters	Amyl formiate, Ethyl acetate, Ethyl propionate
Ketones	Acetone, Methyl ethyl ketone, Mesityl oxide
Halogenated hydrocarbons	Methylene chloride, Chloroform
Iso-alcohols	Isopropanol, Methylbutanol
Ethers	Diethyl ether, Di-isopropyl ether
Other compounds	Carbon monoxide, Oxygen, Nitrogen, Rare gases, Methane, Nitromethane, Carbon disulfide, Dimethyl sulfide, Thiophene

TABLE II

COMPONENTS ADSORBED COMPLETELY ON MOLECULAR SIEVE 5 Å COLUMN

Group	*Components tested*
Normal paraffins (except methane)	Propane, *n*-Butane, *n*-Hexane
Normal olefins	Ethylene, Propylene, Hexene-2
Normal alcohols	Methanol, Ethanol, *n*-Butanol
Aldehydes	Acetaldehyde, Propionaldehyde, Isovaleraldehyde
Acids	Formic acid, Propionic acid

The other types of molecular sieves do not behave similarly, since their pore openings are different. The molecular sieve 4 Å (pore opening of 4 Å diameter) adsorbs only ethane of the *n*-paraffins, with elution of propane and higher members. Of the *n*-olefins ethylene and propylene are adsorbed on the molecular sieve type 4 Å but the butenes and higher are not. The situation is similar with oxygenated compounds: *e.g.* the *n*-alcohols from *n*-butanol pass through this material, because their molecules are larger than 4 Å. Whereas, because of the very large pore openings (about 13 Å), the molecular sieve type 13 X adsorbs practically all organic compounds which are given in Table I (these components pass through the 5 Å molecular sieve

column). Oxygen, nitrogen, carbon monoxide and methane are, furthermore, not adsorbed by this column.

The above illustrates that because of the variety of molecular sieves it is possible to select a given type which retains individual compounds in a sample, while the others pass through the column.

Application of the specific adsorption characteristics of molecular sieves

The specific adsorption characteristics of molecular sieves offer in practice two advantages:

1. In analysis of complex mixtures, containing various series of homologs, the removal of one of these series will serve to quantitatively identify the series, each of the members of the series (since elution time is proportional to carbon number) and finally, indicate the possible identity of non-adsorbed components.

2. The removal of an adsorbable component from a system may permit observation and measurement of peaks otherwise obscured by overlap.

In these applications, the molecular sieve column is to be placed in series with a standard partition column, as shown in Fig. 1. In this case, mixtures of components were injected into the unit and passed first through the molecular sieve column. Here some components were adsorbed and those which passed through were separated by the partition column in the standard manner.

The analysis of complicated hydrocarbon mixtures is a good example for using this technique. In an earlier publication[7] the fractogram of *n*-paraffin subtraction by

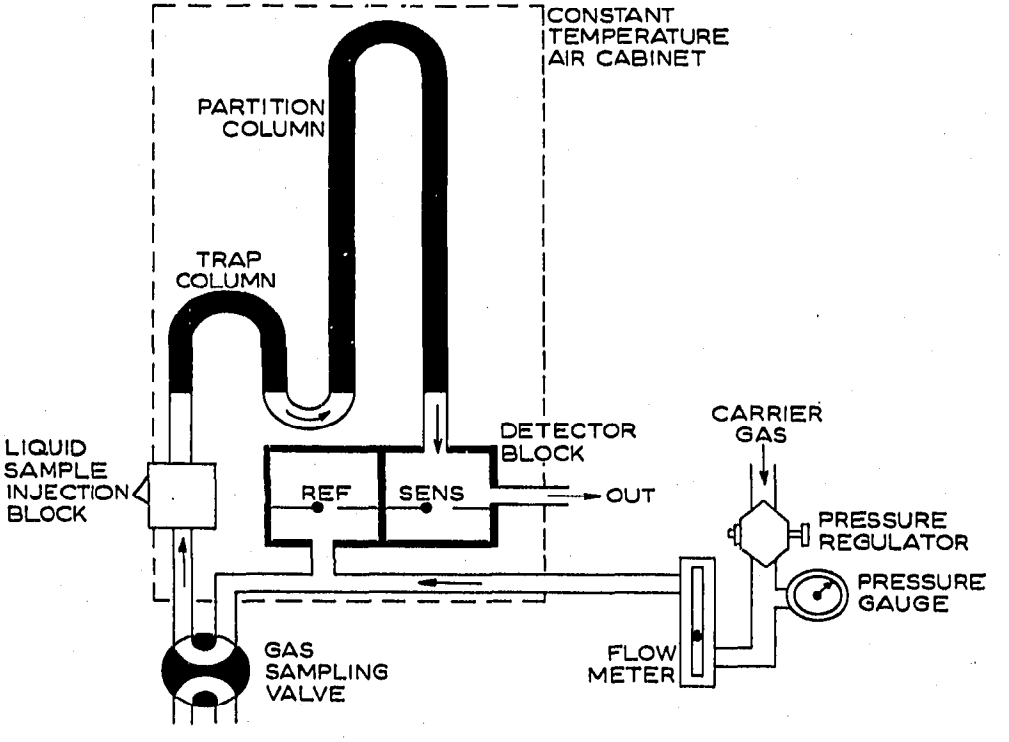

Fig. 1. The use of a molecular sieve column as trap column in the gas chromatograph.

molecular sieves type 5 Å was given. WHITHAM[8] used the same method for the determination of the *n*-paraffins in heavier petroleum fractions.

In other cases, the removal of a component is necessary, which partly overlaps other components in the fractogram. The right part of Fig. 2 shows the fractogram of a mixture containing isopropyl ether, propionaldehyde, acetone, ethyl acetate and ethanol, analyzed on a standard partition column*. As shown, the acetone peak is partly overlapped by the propionaldehyde peak. Using a short molecular sieve 5 Å column in series, the propionaldehyde peak (and the peak of ethanol) is completely removed.

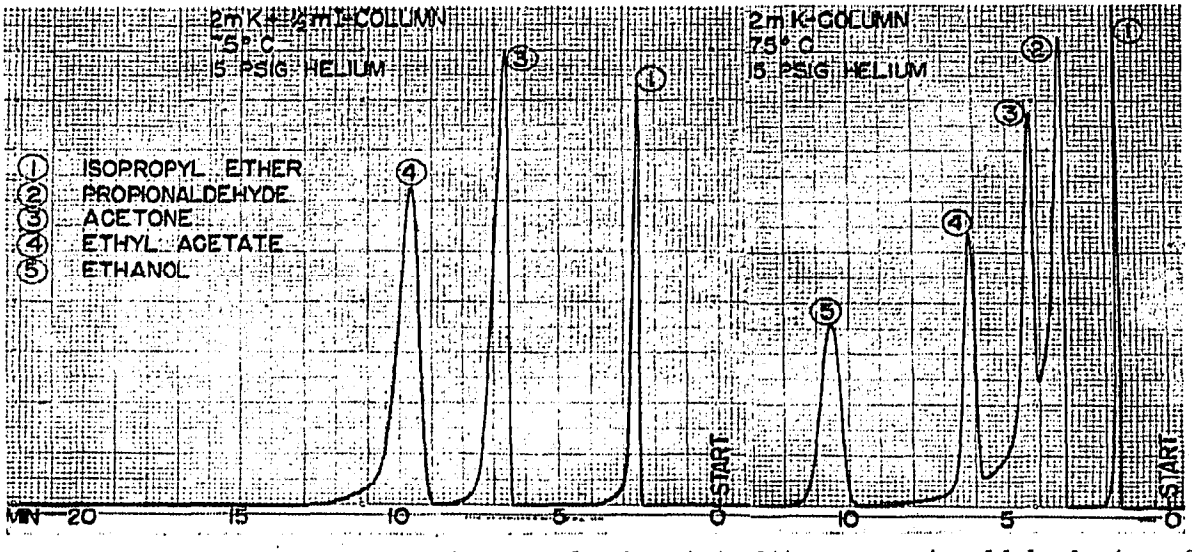

Fig. 2. Analysis of a mixture of: 1, isopropyl ether (16.7 %); 2, propionaldehyde (33.2 %); 3, acetone (16.7 %); 4, ethyl acetate (16.7 %); and 5, ethanol (16.7 %), at 75° and 15 p.s.i.g. helium inlet pressure. Column: at the right analysis, 2 m K; at the left analysis, ½ m I + 2 m K.

Temperature limitations

As shown, the temperature used in this investigation was 100°. Operating at temperatures below 100°, the adsorptive effects of the sieves will result in increasing the retention time of components which would pass through rapidly at higher temperatures. Analyzing *e.g.* a hydrocarbon mixture containing olefins, the iso-olefins such as isobutene are strongly held at 75° or lower even though this class of compound should be eluted. The molecular sieves should therefore be used at high temperatures for subtractive purposes in order to minimize retention time of components which are not irreversibly held. In the case of analyses of light components the sieve column may be heated separately by resistance wire to a level higher than that of the necessarily cool analyzing column.

In the subtraction of *n*-paraffins, temperatures as high as 130° have been used. Even at this elevated temperature, ethane and propane are held for long periods,

* The column designations of the Perkin-Elmer Corporation are the following: Column I: Molecular sieve 5 Å column (20–60 mesh); Column K: 30 weight-% polyethylene glycol (Carbowax 1500) on Chromosorb 30–60 mesh.

while components boiling as high as *o*-xylene are eluted without delay. It might be mentioned that carbon dioxide is eluted at this temperature in 10 minutes.

SUMMARY

The use of Linde Company "Molecular Sieves" in gas chromatography to irreversibly adsorb particular components was discussed. The behavior of various homologous series and special components of general interest on columns run at 100° is shown. Since those compounds not adsorbed pass through with virtually no retention time, they may be conventionally separated by partition on adsorption columns placed in series with the "Sieves". This property may be used to aid the identification of components in unknown samples or for the removal of one component whose elution band overlaps that of a peak of interest. The temperature limitations of their use are discussed.

REFERENCES

1 *Chem. Eng. News*, 36 No. 21 (1958) 62–63; 37 No. 19 (1959) 45.
2 J. JANÁK, *Chem. listy*, 47 (1953) 817; *Collection Czechoslov. Chem. Communs.*, 19 (1954) 684.
3 J. JANÁK, in D. H. DESTY, *Vapour Phase Chromatography*, Butterworths, London, 1957, pp. 247–255.
4 G. KYRYACOS AND C. E. BOORD, *Anal. Chem.*, 29 (1957) 787.
5 H. PIETSCH, *Erdöl u. Kohle*, 11 (1958) 157.
6 N. BRENNER AND E. CIEPLINSKI, *Ann. N. Y. Acad Sci.*, 72 (1959) 705.
7 N. BRENNER AND V. J. COATES, *Nature*, 181 (1958) 1401.
8 B. T. WHITHAM, *Nature*, 182 (1958) 391.