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SOME APPLICATIONS OF MOLECULAR SIEVES IN THE GAS CHROMATOGRAPHIC ANALYSIS OF HYDROCARBONS AND ALCOHOLS*

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SUMMARY

Methods based on the selective adsorption of straight-chain C_9–C_{20} hydrocarbons on 5 Å molecular sieves for quantitative determinations of (1) small amounts of non-linear compounds in *n*-paraffin extracts, (2) *n*-paraffins in kerosene and gas oil and (3) *n*-alcohols in primary oxo-alcohols are described.

The short analysis time permits the application of these methods in the control of the industrial production of high-purity *n*-paraffins and alcohols.

INTRODUCTION

Molecular sieves are being increasingly used in the analytical and industrial fields. From an analytical point of view, the use of 5 Å molecular sieves for the quantitative determination of linear compounds in hydrocarbon mixtures has been known for several years[1–6]. These methods typically employ adsorption of linear compounds in the liquid phase and weighing of the sieves before and after treatment. More recently, gas chromatographic (GC) methods have been described for the determination of small amounts of non-linear compounds in linear hydrocarbon mixtures by their on-column adsorption in the vapour phase[7–9]. Some of these methods employ systems in which chromatograms of both the untreated mixture and the denormalized mixture are recorded. Based on this principle, two methods for the simple and rapid control of the extraction of large amounts of *n*-paraffins from kerosene and gas oil in industrial plants are described in this paper.

EXPERIMENTAL AND RESULTS

Determination of small amounts of non-normal compounds in high-purity n-paraffin extracts in the carbon number range C_{10}–C_{20}

Samples of *n*-paraffin extracts obtained by the Isosiv process based on the

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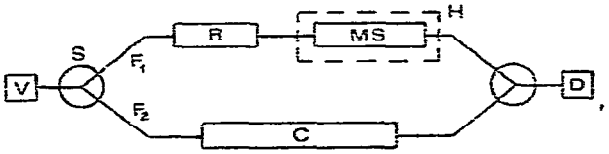

Fig. 1. Gas chromatographic system used for rapid quantitative determinations of impurities in *n*-paraffin extracts. V = sample vaporizer; S = splitter; F_1, F_2 = flows of the split sample; R = retarding column, 0.2 m × 4 mm I.D., 20% SE-30 on Chromosorb P; MS = molecular sieve column, 0.2 m × 4 mm I.D.; H = heating mantle for column MS situated ir the oven of the chromatograph with an accurate temperature controlling device (350 ± 0.3° during operation); C = analytical column, 1.5 m × 4 mm I.D., 20% SE-30 on Chromosorb P; D = flame ionization detector. Oven temperature = 210°.

sorptive action of 5 Å molecular sieves (Union Carbide) have been analyzed for the quantitative determination of small amounts (0.3–1.5%) of non-normal compounds contained as impurities in the final plant products. Although suitable analytical methods have already been described by other workers for this type of determination[7–9], the length of time required for analysis precluded their use in industrial situations. A new GC system has therefore been developed, as shown schematically in Fig. 1.

The sample is injected into the vaporizer V and split into two flows, F_1 and F_2, in a ratio of approximately 2:1. The sample flow F_1 is eluted through the retarding column R, completely denormalized by 5 Å molecular sieves contained in the column MS, and revealed by the flame ionization detector D as one peak; it represents all of the non-normal compounds contained in F_1. The sample flow F_2 flows slowly through the column C and begins to be revealed later than F_1. Therefore, in the final chromatogram (Fig. 2) are recorded a peak (TNN) belonging to the total non-normal components contained in the flow F_1 and after a short delay as many peaks of the flow F_2 as can be separated by the column C.

Quantitative determinations are simple once a response factor F has been determined from the analysis of a standard mixture in which the content of the non-normal components is known. The response factor can be calculated by the equation

$$F = \frac{(\text{Area } F_2) \times (\text{wt.-\% of TNN})}{(\text{Area } F_1)}$$

Once the value of F has been calculated for the pure standard, this equation can be used to calculate the weight percentage of TNN in unknown mixtures. Standard mixtures can be blended using pure compounds or typical extracts.

The constancy of F was verified during a series of analyses, the results and accuracy data for which are given in Table I. The carbon number distribution and content of non-normal compounds may be determined by this method in about 7 min. The carbon number distribution is calculated assuming that the non-normal components are uniformly distributed. Even if this does not occur, considering that the content of TNN does not normally exceed 1.5%, only a relatively small error may be introduced.

Conditioning of sieves. A large number of analyses can be run without regenera-

tion of the sieves and very satisfactory repeatability and constancy of the correction factor are obtained. The correction factor is determined at the beginning and at the end of the series of analyses.

A constant operating temperature of the column containing the sieves of $350 \pm 0.3°$ is maintained during the analysis by means of a heating mantle. In previous work, Gawlik *et al.*[7] indicated that an anomalous adsorption of polar aromatic compounds on the sieves may occur under these conditions. Preliminary deactivation of polar sites that might be present on the surface of new sieves in order to prevent this possibility is therefore useful.

For this purpose, good results were obtained by injecting several microlitres of aromatic compounds, for example aromatic extracts, in new or regenerated sieves under the same operating conditions as used in the analysis. No adsorption of isoparaffins with a long linear chain and a methyl group at one end of the chain occurred. Regeneration of the sieves can be performed at about 400°.

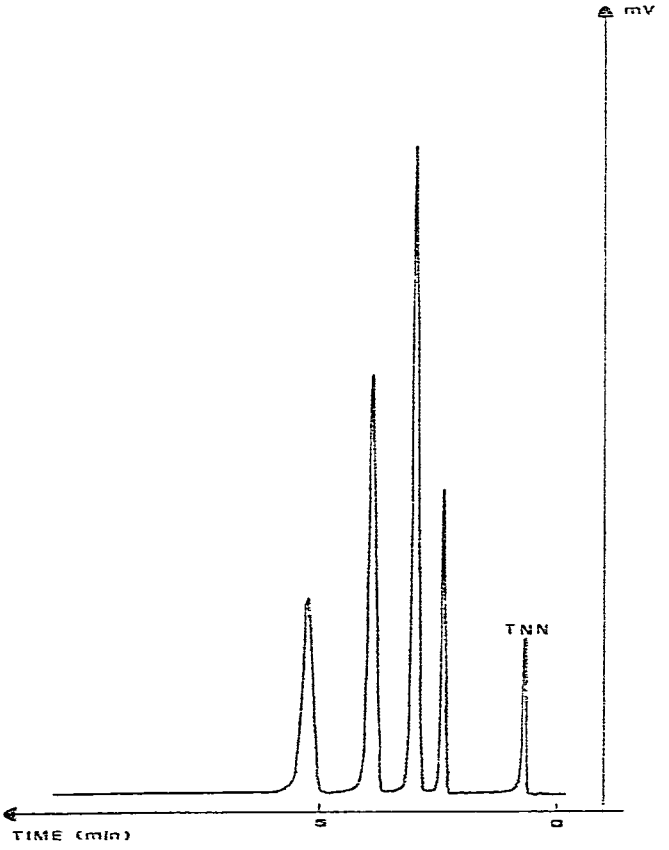

Fig. 2. Gas chromatogram of a typical sample of an *n*-paraffin extract in the range C_{11}–C_{14}, recorded under the conditions of the system shown in Fig. 1. The peak indicated as TNN represents the denormalized (total non-normal) fraction of the split sample F_1 (see Fig. 1). The other peaks represent flow F_2 after passage through the analytical column C.

TABLE I

RESULTS FOR DETERMINATIONS OF IMPURITIES IN *n*-PARAFFINS

Components	*Known composition (wt.-%)*	*Found (wt.-%) (mean values)*	*Relative standard deviation*	*Results for a typical sample (wt.-%)*
Below C_{11}	0.21	0.24	4.8	0.18
C_{11}	23.26	23.20	1.1	23.86
C_{12}	32.81	32.90	1.6	30.24
C_{13}	26.26	26.16	1.2	24.05
C_{14}	15.22	15.26	1.9	20.54
Above C_{14}	0.07	0.07	6.3	0.39
Total non-normal	2.17		6.1	0.74
F		26.19	1.9	

n-Paraffin content in kerosene and gas oil

The problem of the rapid determination of the content of *n*-paraffins in kerosene or gas oil destined for denormalization plants for the production of high-purity *n*-paraffins has been considerably simplified by using the GC system shown in Fig. 3.

The sample is injected and almost immediately detected by detector 3, after a short delay due to its passage through the capillary tube 2. All of the sample injected is therefore recorded as one peak. Its flow then slows during its passage through columns 4, 5 and 6. Pre-treated molecular sieves denormalize the sample in column 6. The detector 8 reveals with reversed polarity a second peak, which represents the denormalized sample. The difference between the areas of the first and second peaks represents the amount of linear compounds contained in the sample.

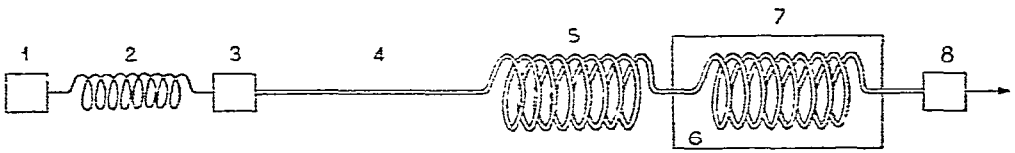

Fig. 3. Gas chromatographic system for determinations of linear compounds contained in kerosene and gas oil. 1 = Injector; 2 = capillary tube, 1 m × 0.5 mm I.D.; 3 = thermal conductivity detector (polarity +); 4 = column filled with P30–60, I.D. 1/8 in.; 5 = column filled with 10% OV-1 on Chromosorb W, 1.5 m × 1/8 in. I.D.; 6 = column filled with pre-treated 5 Å molecular sieves, 1/8 in. I.D.; 7 = heating oven for the column containing the sieves situated in the oven of the gas chromatograph with an accurate temperature controlling device (360 ± 0.3° during operation); 8 = thermal conductivity detector (polarity −). Oven temperature = 270°.

In order to verify the efficiency and selectivity of the sieves, a standard sample of known composition has to be run before a series of analyses is carried out. The percentage of non-linear components in the sample is simply obtained by multiplying by 100 the ratio (area of non-linear components)/(area of total sample). A typical chromatogram of kerosene recorded under these conditions is shown in Fig. 4.

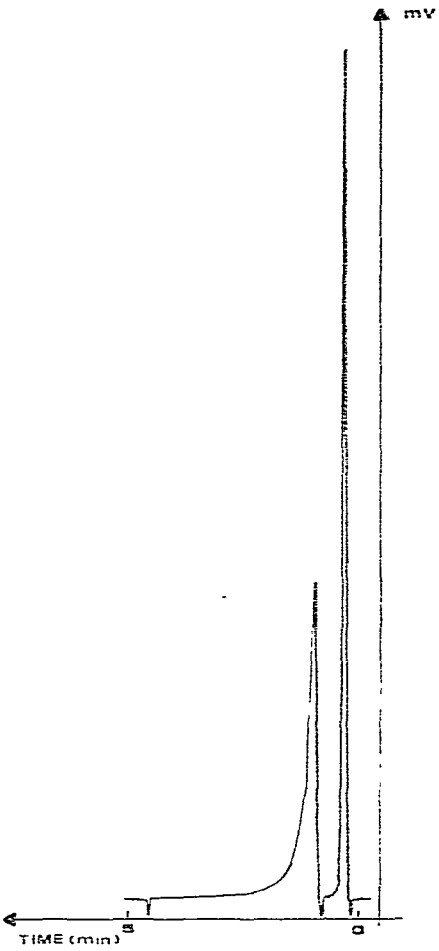

Fig. 4. Typical chromatogram of kerosene recorded under the conditions of the system shown in Fig. 3. In chronological order, the first peak represents the injected sample and the second the denormalized sample. Between them, inversion of polarity and adjustment to the baseline can be observed.

After having recorded the first peak, the polarity of the thermal conductivity detector must be reversed and the pen adjusted to the baseline. Manual positioning of the integrator is required for the integration of the second peak. In the experience of the authors, this system is useful for the rapid control of kerosene and gas oil feedstocks and of the amount of residual *n*-paraffins in denormalized kerosene or gas oil during the industrial productions of high-purity *n*-paraffins. The time of analysis is only 5 min. It is clear that the advantages deriving from such a short analysis time must be balanced against the lack of other types of information and qualitative data. Typical results and comparisons with samples of known composition are given in Table II.

Conditioning of sieves. Before use, the molecular sieves (5 Å, 30–60 mesh) must be pre-treated with aromatic compounds, possibly of the same type as the

TABLE II

RESULTS FOR CONTENT OF *n*-PARAFFINS IN TYPICAL SAMPLES

Sample	*Content of n-paraffins (wt.-%) (known composition)*	*Content of n-paraffins found (wt.-%)*	*Relative standard deviation*
Kerosene	26.91	27.13	1.3
Denormalized kerosene	4.86	4.60	2.6
Gas oil	23.65	22.66	2.0
Denormalized gas oil	1.75	1.10	6.2

sample that is to be analyzed. As pointed out above, the sieves could exhibit an affinity for some aromatic compounds contained in the sample (particularly naphthalenes). This effect would decrease the signal of the second peak in the chromatogram (non-normal peak).

Pre-conditioning of the sieves can be accomplished by washing them with heavy aromatics or by injecting 10 μl of heavy aromatics 10–15 times before beginning the analysis. Aromatics can be extracted by percolation through silica gel or obtained from the heavy components of the Udex process.

Determination of linear components in primary alcohols derived from oxo-formylation of internal double bond (random) linear olefins (cobalt base catalyst)

The procedures of "vapour phase" denormalization in a GC column as shown in the previous examples cannot be applied to alcohols in the same carbon number range, as the use of high-temperature columns filled with molecular sieves produces dehydration of alcohol mixtures. Therefore, the adsorption of linear alcohols by the

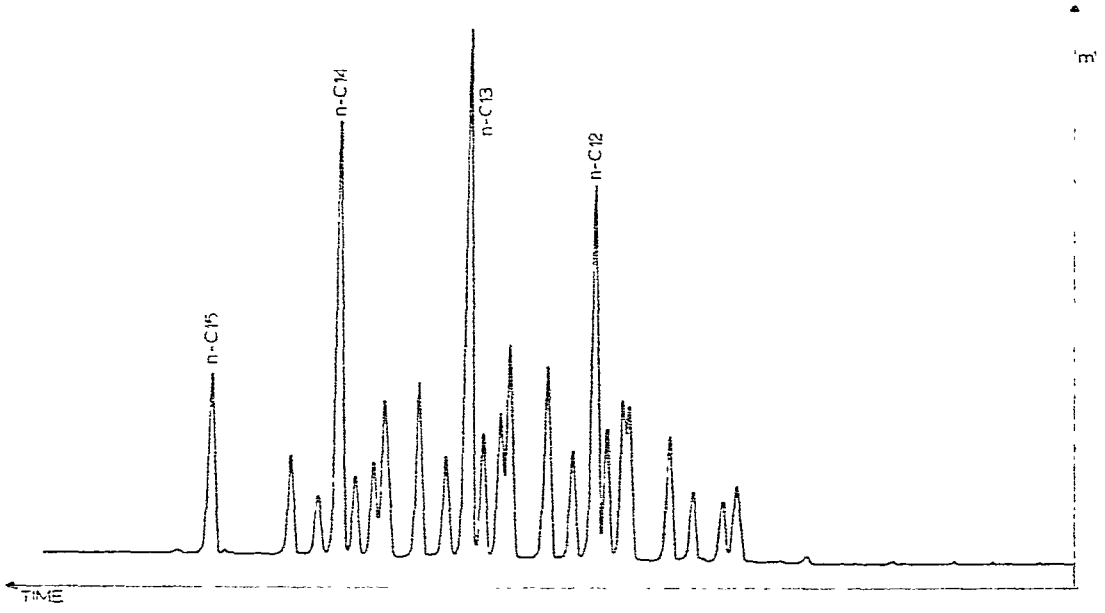

Fig. 5. Capillary column chromatogram of a typical sample of oxo-alcohols in the range C_{12}–C_{15}.

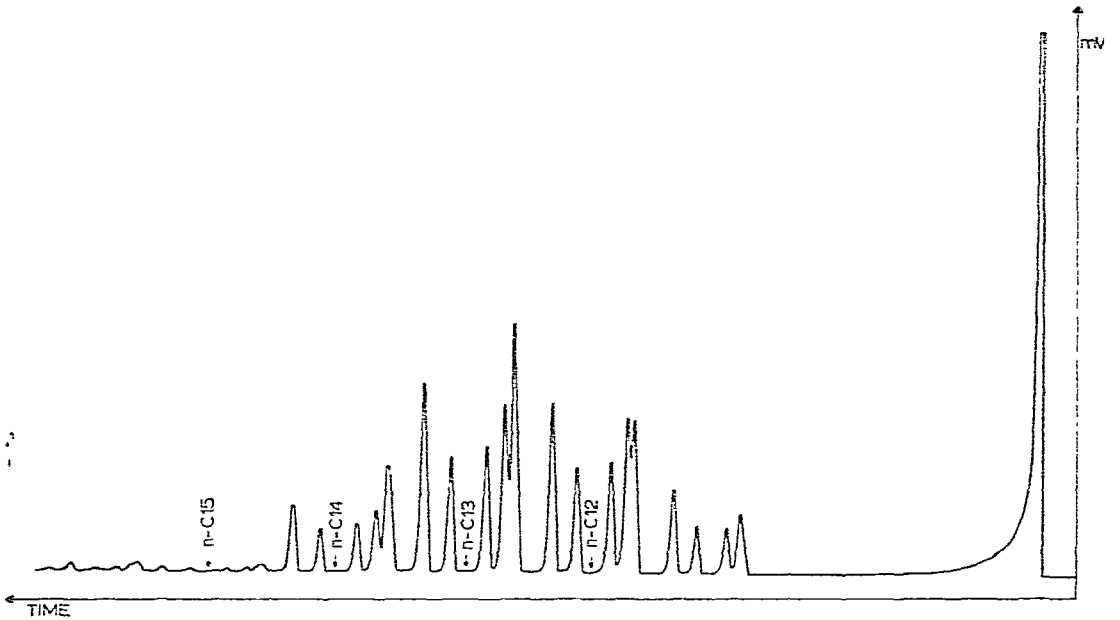

Fig. 6. Capillary column chromatogram of the sample as in Fig. 5, after treatment with molecular sieves.

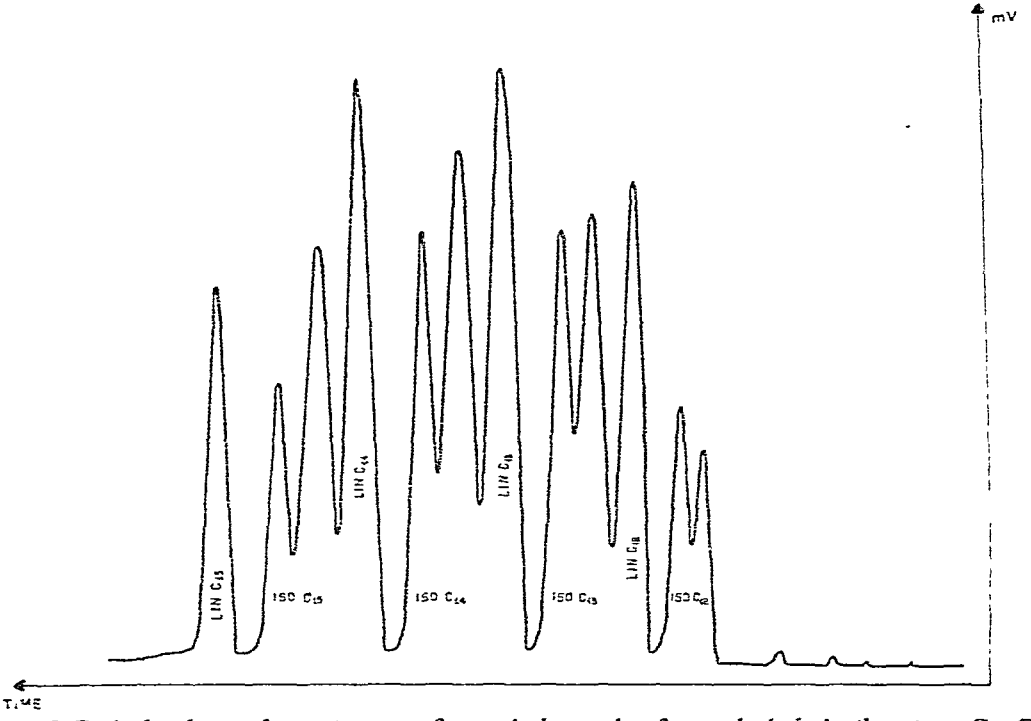

Fig. 7. Packed column chromatogram of a typical sample of oxo-alcohols in the range C_{12}–C_{15}. Linear compounds, iso-compounds and carbon number are indicated. Traces of paraffins are present. Column, 2.5 m × 1/8 in. I.D., 10% UCC W 98 on Chromosorb AW-DMCS. Oven temperature = 130–180° at 2°/min. Normal alcohols are indicated as lin C_x, where x is the carbon number.

use of molecular sieves is performed by traditional solid–liquid-phase methods. Mixtures of linear and isoalcohols of the type $R \cdot CH(R') \cdot CH_2OH$, where R is a linear hydrocarbon chain and R′ is a linear hydrocarbon chain or hydrogen in the case of linear alcohols, derived from the oxo-formylation of linear olefins with the double bond in random positions, have been analyzed by low- and high-resolution GC in order to determine the content of linear compounds for the purpose of plant control. The capillary column gas chromatogram of a typical acetylated C_{12}–C_{15} alcohol mixture is shown in Fig. 5. Fig. 6 represents the same sample after denormalization by molecular sieve adsorption of linear compounds. The peaks indicated as "*n*-C*x*" have been identified as the acetylated linear primary alcohols with *x* carbon atoms. The other peaks correspond to the derivatives of isoalcohols as determined by gas chromatography–mass spectrometry[10]. For the same carbon number, the isocompounds appear in the chromatogram before each linear compound. Peaks belonging to impurities of paraffins and the solvent peak (Fig. 6) are also present in the chromatograms.

Although the quantitative determination of the content of linear compounds could be possible by this means, other experiments were carried out in order to reduce the time of analysis and to verify the efficiency of adsorption of linear alcohols by the sieves. It was found that an almost complete separation of linear alcohols from iso-

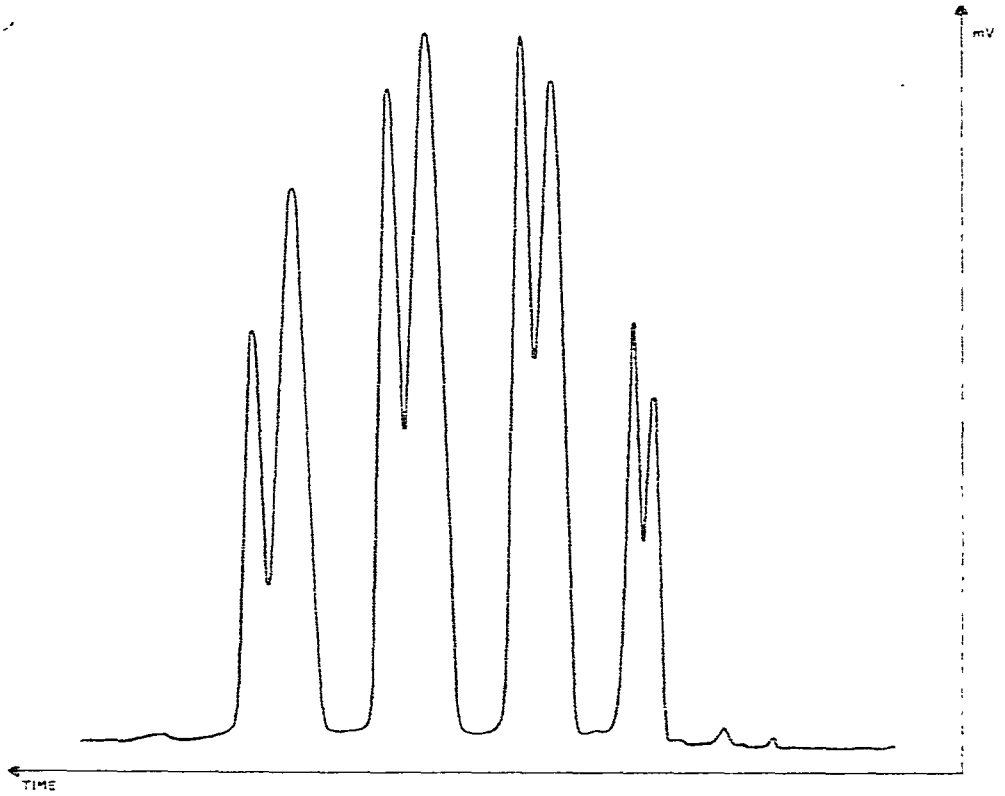

Fig. 8. Packed column chromatogram of the sample of oxo-alcohols shown in Fig. 7 after adsorption of linear compounds.

alcohols is possible even using a packed column without previous acetylation. Integration can be conveniently accomplished using integration limits as shown in Fig. 7. Comparison of the results obtained by analyses with capillary and packed columns shows good agreement for both the carbon number distribution and the content of *n*-alcohols.

Adsorption of linear alcohols and analyses of the separated products. Molecular sieves dried at 400° for 4 h in a flow of dry nitrogen were added in a ratio of 10:1 with the sample in isooctane (spectrophotometric grade, Carlo Erba, Milan, Italy) solution. Refluxing for 16 h completed the adsorption of linear compounds. Very careful washing of the sieves was necessary in order to remove all non-normal compounds.

The chromatogram of non-normal alcohols after treatment with molecular sieves is shown in Fig. 8. The same analytical conditions were used to obtain the chromatograms shown in Figs. 7–9.

The analysis of the compounds adsorbed by the sieves was performed by destroying the sieves with hydrofluoric acid, extraction and then analysis of the adsorbed substances by GC. An almost isomer-free chromatogram is obtained (Fig. 9). Superimposition of the chromatogram of Fig. 8 on to Fig. 9 gives the chromatogram

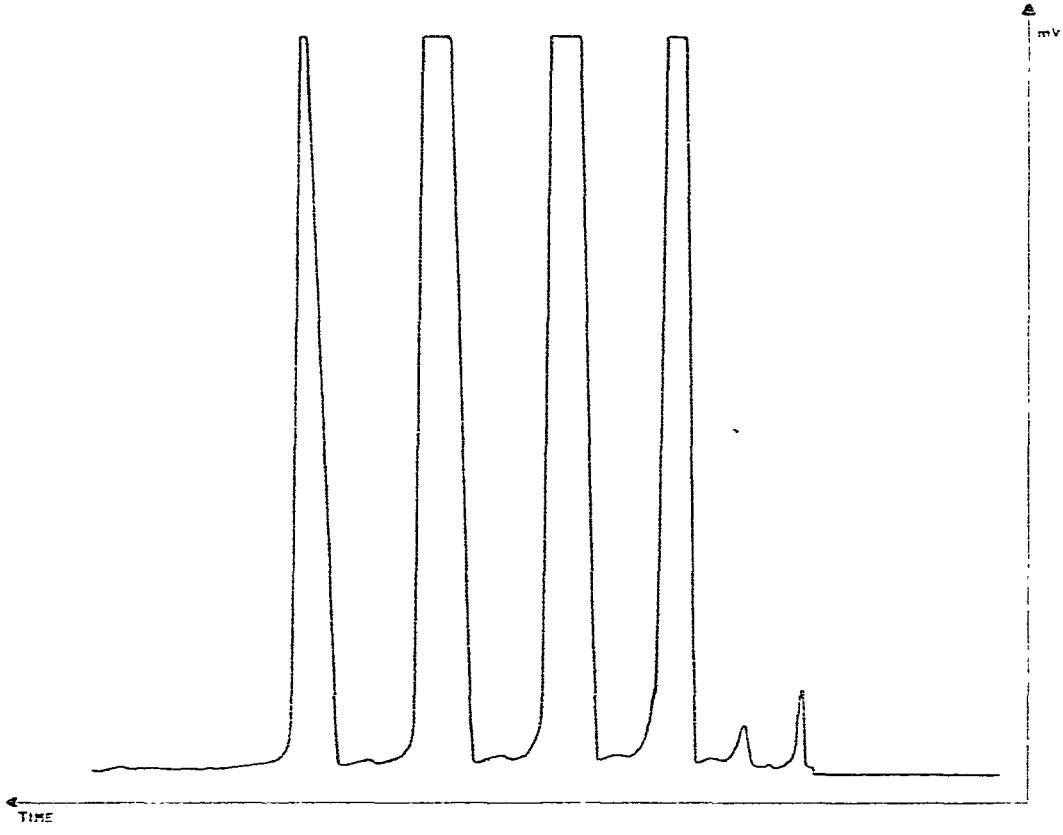

Fig. 9. Packed column chromatogram of the linear alcohol adsorbate.

of Fig. 7 with a 3–4% relative accuracy for the carbon number distribution and isomer content.

It was also demonstrated that only linear alcohols are adsorbed by the sieves; no isomers were detected in the high-resolution gas chromatogram of the acetylated adsorbate.

Further, the analysis of the chemically reduced adsorbate (paraffins) revealed no appreciable content of isoparaffins. The reduction procedure has been accurately tested[11].

It can be concluded that the packed column analysis of the alcohol mixtures examined is a sufficiently accurate and rapid method for determining the carbon number distribution and isomer content. Further, it has been verified that the adsorption of *n*-alcohols is highly selective.

CONCLUSIONS

GC methods for determining *n*-paraffins in mixtures of hydrocarbons have been developed. Although maximum information cannot be obtained from the chromatograms, the short time of analysis can be useful for controlling the content of *n*-paraffins in feedstocks and the purity of the *n*-paraffin extracts in the Isosiv process. Further, some aspects of the adsorption of linear alcohols by 5 Å molecular sieves in the solid–liquid phase connected with GC applications have been demonstrated. A high selectivity for *n*-alcohol adsorption in comparison with all isoalcohols has been demonstrated.

The experiences of other workers concerning adsorption of "polar" hydrocarbon compounds (aromatics), probably on the surface of the sieves, under GC conditions have been verified.

Substantial adsorption of iso-compounds that have a long linear hydrocarbon chain and a 2-methyl group has not been verified either for hydrocarbons or for primary alcohols under the analytical conditions used.

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