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COMBINATION OF RECTIFICATION AND GAS CHROMATOGRAPHY FOR SEPARATION OF MULTICOMPONENT MIXTURES OF COMPOUNDS ACCORDING TO BOILING POINTS

ILMAR KLESMENT
Institute of Chemistry, Estonian Academy of Sciences, Academy Street 15, Tallinn 26 (U.S.S.R.)
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SUMMARY

A simple and effective substitute for laboratory rectification apparatus is described. In the apparatus rectification is combined with preparative gas chromatography, a mixture boiling in a wide temperature range being first separated in the rectification column and then continuously fed as distillate during the whole fractionation cycle into the chromatographic column. The temperatures of rectification and of the chromatographic columns follow the same increasing linear programme. Steam, used as carrier gas, passes through both columns and is condensed together with the separated fractions. The vapours are drawn through the columns by a vacuum at the end of the device.

The apparatus can be used to fractionate petroleum and liquid by-products of coking and synthesis.

INTRODUCTION

Since the invention of gas chromatography (GC) the application of rectification techniques for analysis of multicomponent mixtures of volatile compounds has lost much significance. In both methods separation basically proceeds according to the vapour pressures of the components, but the separation efficiency of GC is higher and components can be separated according to their chemical properties using stationary phases of different polarities. The effect of the change in component activities in the presence of a high-boiling liquid is also used on a limited scale in extractive distillation.

The disadvantage of the rectification method is its low separating efficiency: ordinary laboratory rectification columns have no more than 40–70 theoretical plates (TP), and a separation cycle lasts 1–3 days. Especially time consuming is the establishment of equilibrium during the starting period for the distillation of microquantities (up to 50 ml).

The GC method is characterized by high efficiency, even short columns with a length of 1 m often having more than 1,000 TP. Here it is necessary to note that the TP efficiencies in GC and in rectification are not equal[1]. In GC reflux is not used (each TP is used only once), resulting in a lower practical efficiency of TP than in rectification. In spite of this the separation power of GC apparatus greatly exceeds that of an ordinary laboratory rectification device.

In the case of GC the cycle is short and does not exceed a couple of hours. The disadvantage of the method is its low productivity, only a few milliliters even with preparative apparatus. In the analysis of petroleum and coking by-products rectification techniques are used to obtain data on the fractional composition (distribution of components by boiling points) and to obtain samples of fractions for further analysis. For the substitution of the rectification method a simulated distillation method applying GC techniques has been developed[2–4].

Applying low efficiency GC columns with a non-polar liquid phase and temperature programming, it is possible to obtain data on the fractional composition of petroleum crudes boiling in a wide range of temperature (50–500°). In this way, however, it is impossible to obtain more information about the composition of fractions, since the amounts separated do not exceed a few milligrams.

Temperature programming in preparative GC permits the separation of substances in larger amounts than is possible under isothermal conditions[1]. Thus in a 6.6 m × 9 mm I.D. column containing 30% SE-30, 7 ml of methyl esters of C_6–C_{18} fatty acids were separated[5].

EXPERIMENTAL

Principles of operation

The aim of the present work was to develop a method for the separation of mixtures boiling in wide temperature ranges into narrow boiling fractions in amounts sufficient for further analysis by various chemical and physicochemical methods. The problem was how to combine the high separating efficiency of GC with the higher throughput of a rectification apparatus.

A preparative GC column was used with slow-speed temperature programming and, consequently, a relatively long working cycle. For enhancing the productivity of the GC column and for eliminating overload of its initial part an essential innovation was used: the substance to be separated was subjected to rough preliminary fractionation in a rectification column and subsequently, during the working cycle, passed into the GC column. As we know, in the course of ordinary column temperature programming, the components remain in the initial part of the column until the temperature is optimal for their separation from higher and lower-boiling constituents. When the components enter the column a little prior to this critical moment, their separation is improved considerably, as in this case the initial part of the GC column is not just a sample depository but actively promotes separation.

To simplify the method and apparatus some alterations were introduced: steam was used as carrier gas for GC separation and gas phase movement in the system did not proceed under the influence of pressure, as usual in GC, but as a result of a vacuum at the end of the system.

A number of investigators have used steam as the carrier gas in analytical GC[6–8]. It is supposed that steam decreases the adsorption of components[6], thus improving the separation of high-boiling polar compounds. Steam can be condensed together with separated components and therefore there is no escaping gas and no sample loss. However, as steam liquifies at a low temperature it sets limits to its application for separation of low-boiling components.

Vacuum considerably reduces the emergence temperature of components and enables the chromatographic separation of high-boiling compounds. According to Palamand and Thurow[9] high vacuum is supposed to reduce the column efficiency, but contradictory views have also been published[10].

Apparatus

The apparatus is shown schematically in Fig. 1. Steam was taken from the vapour phase of water boiling in a flask under condenser by a copper pipe, I.D. 1.5 mm. At one point the pipe was flattened to form a throttle to control the amount of steam entering the separation column system. Throttles with different resistances were used. Steam entered a distillation flask of effective capacity 25 ml. The flask was connected to a Vigreux rectification column (height 40 cm). Its separating efficiency, according to published data[11], was 7–10 TP. The temperature of the flask was raised synchronously with the temperature of the succeeding GC column and it was held, depending on the amount of steam and temperature programming speed, 10–30° lower than the temperature of the GC column. The rectification column acted simultaneously as a partial condenser as well, its temperature being regulated so as to provide the formation of reflux.

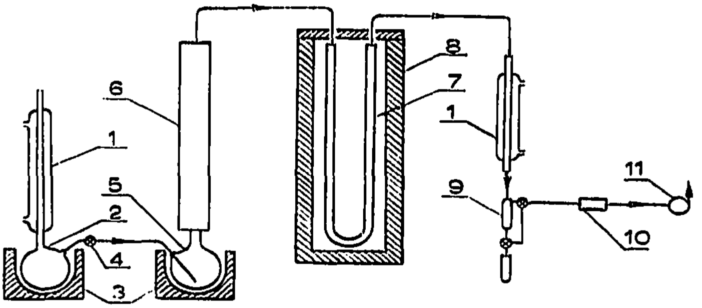

Fig. 1. Fractionating device combining rectification and GC methods. 1 = Water condenser; 2 = flask for steam generation; 3 = electrical heater; 4 = throttle for regulation of steam and creation of vacuum; 5 = flask for sample evaporation; 6 = rectification column; 7 = GC column; 8 = thermostat; 9 = vacuum receiver; 10 = manostat; 11 = vacuum pump.

Partially separated compounds in steam entered the copper GC column, 2.8 m × 12 mm I.D. It was packed with 340 ml of Rysorb C, 0.3–0.4 mm, impregnated with 30.6 g of Apiezon L (21 % of support weight). An isolated thick-walled aluminium tube, with heating windings, was used as a thermostat. The temperatures of all heaters were hand controlled by means of laboratory transformers. Separated compounds and steam emerging from the GC column were liquified in a water condenser and collected in a Labor (Budapest, Hungary) semimicro-receiver. The fractions (0.2–1.0 ml) were taken at equal intervals (5–15 min). Vacuum created by the water pump was maintained by means of a manostat regulator at a residual pressure of 50 mm Hg. At this pressure steam was completely condensed.

TABLE I

SEPARATION CHARACTERISTICS OF HYDROCARBON BLEND AND SHALE SEMICOKING TARS

Assay No.	*Substance*	*Charge (ml)*	*Recovery (ml, and % in brackets)*	*Experiment duration (h)*	*Sampling interval (min)*	*Number of fractions*	*Temperature programming rate (°C/h)*	*Steam consumption (g/h)*	*Steam and distillate ratio*	*Steam inlet (torr)*	*Resolution quality*[*]
1	Hydrocarbon blend	10	8.72 (87)	3.5	10	16	20	15	6:1	488–515	+ + +
2		10	9.00 (90)	3.0	10	15	30	15	4:1	488–515	+ +
3		10	8.88 (89)	2.2	10	12	55	33	8:1	720	+ +
4		10	9.42 (94)	2.7	7.5	21	44	8.9	3:1	410–430	+ +
5		20	18.3 (91)	2.7	7.5	22	41	8.3	1.5:1	410–430	+
6		15	18.2 (91)	2.8	7.5	20	39	7.8	2:1	410–430	+ +
7		10	9.11 (91)	3.5	10	17	22	9.1	4:1	410–430	+ + +
8	Estonian shale semicoking tar	25	9.45 (38)	4.5	15	14	15	16	6:1	488–515	+ + +
9		25	20.9 (84)	5	7.5	30	20	15	5:1	488–515	+ +
10	Sangruntau shale semicoking tar	25	12.9 (52)	5	7.5	31	20	15	8:1	488–515	+ + +

[*] + + + = good; + + = fair; + = poor.

Experiments with a mixture of n-paraffins and n-olefins

To establish the optimum parameters of the unified rectification–GC separation the influence of load, programming rate and the amount of steam on separation accuracy was determined. The subject of experiments was a mixture of normal C_8–C_{15} hydrocarbons isolated from Estonian shale low-temperature carbonization oil by carbamide extraction. For monitoring large amounts of material by GC without raising the throughput rate it is necessary to extend the work cycle, *i.e.* to raise the column temperature slowly. But at a very slow programming speed, as a result of prolonged feeding, the zones of single components in GC column widen and their separation deteriorates.

The results of a number of experiments are presented in Table I. As the purpose of the investigation was the determination of boiling temperatures of fractions it was necessary to calibrate the apparatus with standard substances with known boiling points. For example, *n*-paraffins are suited for the purpose. The calibration results are presented in Fig. 2 as the retention temperatures of hydrocarbons plotted against their boiling points at atmospheric pressure.

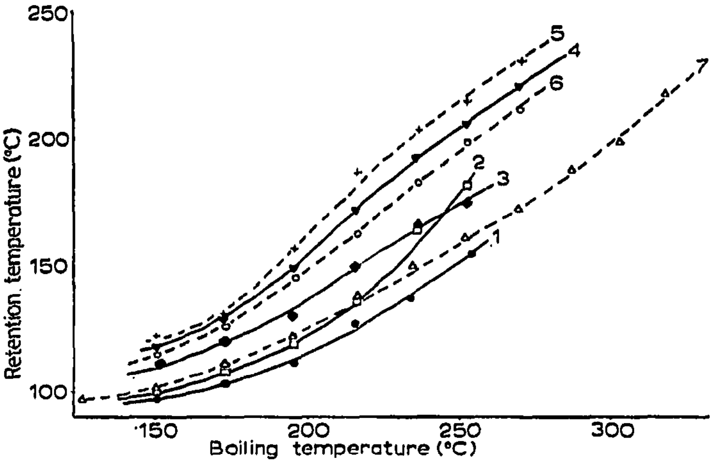

Fig. 2. Dependence of retention temperature of normal paraffins and olefins upon their boiling points and separation characteristics. For fractionation conditions see Table I.

The composition of the fractions obtained was determined on a Chrom-3 chromatograph using a 4 m × 2.5 mm I.D. column containing 5% of Apiezon L on Chromosorb G. The chromatograms of fractions from assay No. 7 (Table I) are presented in Fig. 3, and the rectification curve, representing experimental data, in Fig. 4. In the course of GC separation of homologous straight-chain hydrocarbons, paraffins and the corresponding 1-olefins emerge in pairs, whereas the 1-olefin as a lower boiling point compound appears first. As the boiling points of the succeeding homologues differ considerably, approximately 90% of their potential content is recoverable in the form of separated compounds. Intermediate fractions containing adjoining homologues constitute a negligible amount. Paraffins are not separated from the corresponding 1-olefins, although some accumulation of olefins is observed in the first fractions of each zone.

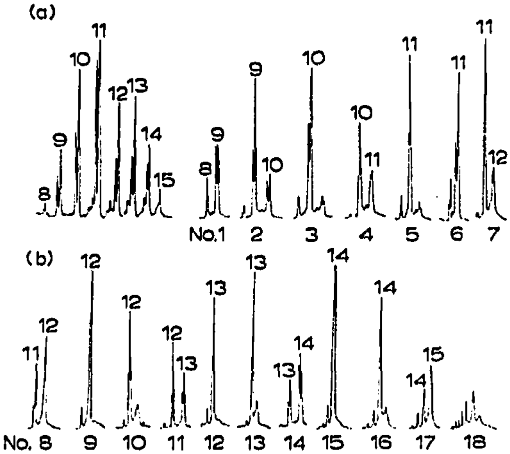

Fig. 3. Chromatograms of (a) paraffin and 1-olefin standard and (b) fractions obtained in assay No. 7 (Table I). Peak numbers correspond to the number of carbon atoms (carbon number) in the molecule of the hydrocarbon. The peak of 1-olefin precedes the peak of paraffin with the same carbon number.

To avoid condensation of steam the initial temperature of the GC column must not be lower than 100° and during the fractionation of the paraffin–olefin standard, therefore, the first fractions were eluted under nearly isothermal conditions. Therefore the relationship between the boiling points of compounds boiling up to 150° and their retention temperature is not linear. Higher-boiling compounds emerge, depending upon working conditions, at temperatures 100° lower than their boiling points.

In the rectification column the process proceeds in a low vacuum, but the

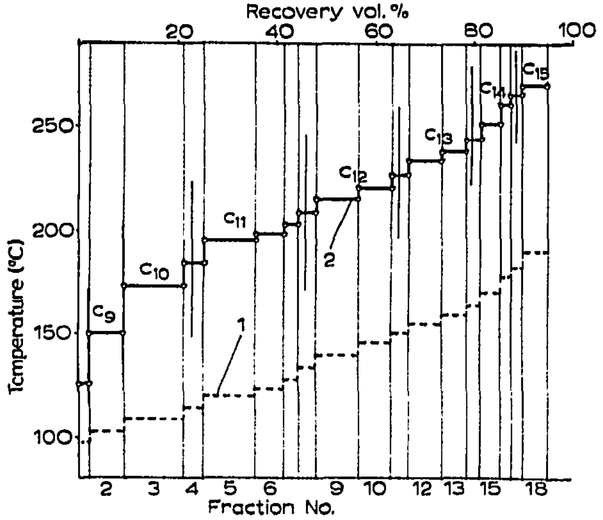

Fig. 4. Rectification curve of a mixture of normal hydrocarbons (assay No. 7). 1 = Temperature of fraction emerging from GC column (retention temperature) and 2 = boiling temperature of fractions at atmospheric pressure.

amount of steam present is considerable. The combination of both factors is in some cases used for the reduction of components' boiling temperatures[12]. By ordinary rectification the consumption of steam does not exceed the amount of distillate, but the GC method requires considerably more carrier gas. According to Krell[11], a high steam concentration reduces the rectification efficiency of the column. In the present work, using high steam to sample ratios, it was necessary to considerably reduce the temperature of the rectification column to provide the necessary amount of reflux. High steam to sample ratios cause other difficulties too, as at low temperatures steam condenses in the flask and the separation of layers in the receiver is complicated. Therefore both high (30 g/h) and low (7 g/h) steam sample ratios deteriorate separation parameters.

The optimum temperature programming rate depends on many complicated factors. In most cases fair resolution was achieved by raising the temperature at a rate of 20–40°/h.

A practical example of the method

The low-temperature carbonization tar of Sangruntau (Kazakh S.S.R., U.S.S.R.) oil shale has a considerable content of high-boiling compounds. Therefore almost half of it remains in the flask as distillation residue (see Table I, assay No. 10). The boiling points of fractions and some physicochemical data are presented in Fig. 5. When the boiling temperatures of fractions rise, the content of aromatic hydrocarbons and cyclic sulphur compounds (tar contains 7% of sulphur) rises quickly, leading to an increase in the specific gravity and refractive indices of the fractions.

The chromatograms of the total tar and some of its fractions are shown in

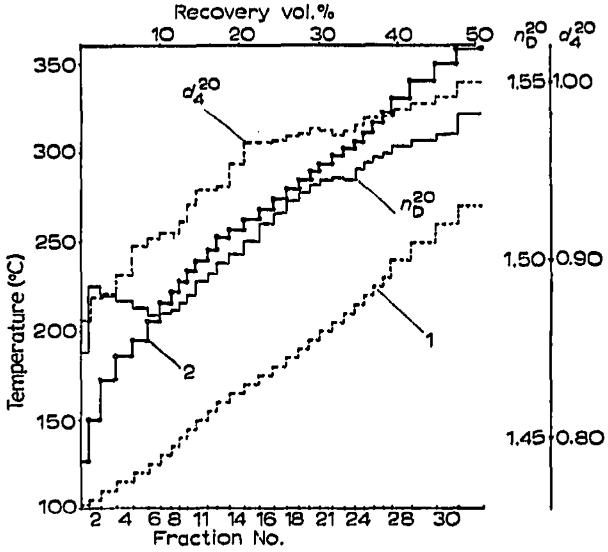

Fig. 5. Rectification curve of low-temperature carbonization tar of Sangruntau oil shale and some characteristics of fractions (assay No. 10 in Table I). 1 = Retention temperature of fractions; 2 = boiling temperature of fractions at atmospheric pressure; d_4^{20} = specific gravity and n_D^{20} = refractive index.

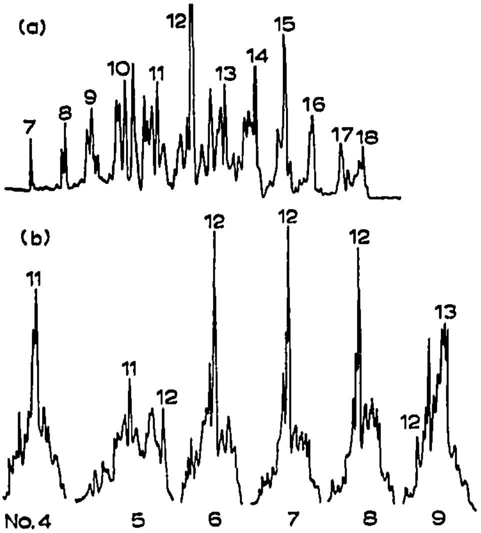

Fig. 6. Chromatograms of (a) Sangruntau oil shale carbonization tar and (b) fractions 4–9. Peak numbers correspond to the number of carbon atoms in the *n*-paraffins.

Fig. 6. Peak No. 12 is high. It is present in three succeeding fractions, amounting to 1.5 ml. The analysis of the fractions in a column with a polar stationary phase revealed that *n*-dodecane, *n*-dodecenes and some aromatic and sulphur containing compounds correspond to peak 12.

DISCUSSION

In the rectification of mixtures of compounds which belong to different groups, azeotropes are formed and as a result the compounds are not separated according to their boiling points[11]. GC is free of the azeotropic effect, but it should be noted that even on non-polar stationary phases the retention temperature of components is also slightly affected by their group properties. Only components with similar properties (*e.g.* hydrocarbons and petroleum) are resolved exactly according to their boiling points.

The compounds boiling below 150° are separated in nearly isothermal conditions. The analysis of low-boiling fractions showed, however, that this does not reduce the accuracy of components separation. Under the conditions used in this work it was possible to separate the compounds boiling up to 400°.

As the separated components are condensed together with steam they must not contain considerable amounts of water-soluble compounds. Instead of steam the vapour of other liquids may be used, for example the separation of glycols may be performed in paraffin hydrocarbon vapours. The use of vapours of organic compounds as carrier gases has already been studied[13,14].

The fractionation apparatus is of a simple construction and is easily built. No detector was used in this work, as it would have been more complicated than the rest of the device, and for obtaining fractions according to boiling points there was no need for it.

The experiments demonstrated that the consumption of steam must exceed the amount of received fractions 4–5 fold, and the optimum temperature programming rate of the GC column was 30°/h. As the temperature increases slowly, preparative columns with larger diameters may be used.

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