Analysis of Rums with a Preparative-Capillary System Employing a Newly Developed Trap-Splitter[1]

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ABSTRACT

Commercial rums were analyzed by means of a trap-splitter developed in the Rum Pilot Plant, interconnected with a 3 m × 12.7 mm o. d. stainless steel 316 column packed with 10% Carbowax 20M on acid washed 60/80 mesh Chromosorb W, and a 91 m × 0.25 mm i.d. stainless steel 316 capillary Golay column coated with polyethylene glycol (ucon) 75 H 90,000. The preparative column, located in a different chromatograph, was used to prepare concentrated fractions of rums which separate either prior to ethyl alcohol or after isoamyl alcohol. After collection in the gas chromatographic preparative trap-splitter, sensitive independent separations of both fractions with the trap-splitter and the capillary Golay column showed at least 10 congeners with retention times lower than that of ethyl alcohol, and about 50 congeners beginning with isoamyl alcohol.

INTRODUCTION

Distilled alcoholic beverages contain large numbers of congeners, but only a few are found at a sufficiently high concentration for accurate detection by direct injection with regular analytical gas chromatography (4, 9). Most congeners, especially those present at concentration below 10 p/m, are analyzed by intricate procedures, usually involving pre-concentration techniques prior to gas chromatographic separation (3). For this purpose, investigators have employed several treatments, such as distillation, solvent extraction, evaporation, neutralization, regeneration, formation of derivatives and precipitation of groups of compounds with a specific reagent (5, 6, 9). Other workers add separation with preparative gas chromatography to the extraction procedures in order to increase the concentration of components, and to collect specific fractions of emerging extracts (7, 8, 11).

Analytical techniques for complete determination of congeners in commercial rums have been used previously (2, 8, 9). Maarse and ten Noever de Brauw (9) removed the congeners in aqueous Jamaican rum with pentane-ether; then the solvent was partially distilled off in a fractional distilling column. The extract was prefractioned in packed preparative columns and further separated in Golay capillary columns. Liebich et al. (8) used condensation of head space vapor and solvent extraction with pentane-ether and pentane to separate a large number of congeners in Jamaica rum. These included esters, acids, alcohols, phenols, lactones, carbonyl compounds, acetals, pyrazine derivatives, thioesters, and hydro-

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carbons, in concentrations ranging from 0.01 to 800 p/m.

Development of preparative-capillary gas chromatographic systems suitable for better separations of congeners in rums without pretreating the samples prior to the analysis, was reported in a previous paper (2). It was feasible to reach a rapid separation of congeners in trace concentrations by injecting the rum samples directly into a preparative column, and subsequently analyzing the collected fractions with a capillary Golay column. However, coupling of a preparative to a capillary column could not be done effectively because of uneven working temperatures, different flow rates and pressures, and large differences in the amount of samples required for both types of chromatography.

In the investigation reported here these problems were overcome by

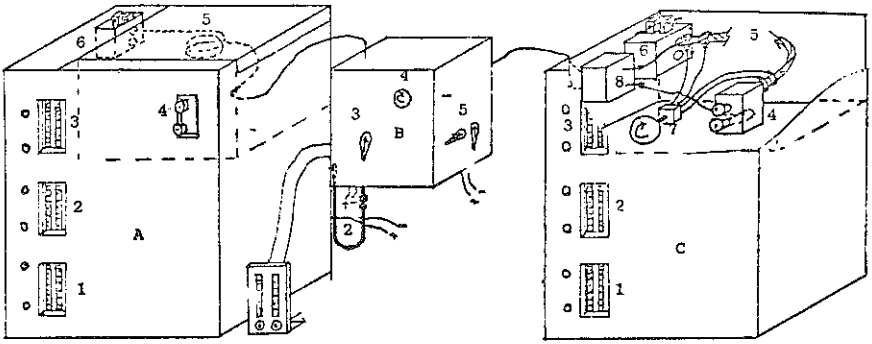

FIG. 1.—Gas chromatographic system for coupling capillary to preparative columns; A and C oven modules 5750 and 5754B gas chromatographs (1—carrier flowmeter; 2—air flowmeter; 3—hydrogen flowmeter; 4—injection port; 5—column; 6—FID; 7—backflush valve and 8—TCD). B Trap-splitter (1—carrier flowmeter; 2—trap; 3—expander valve; 4—splitter valve; 5—inlet and outlet valves).

the use of a compact trap-splitter unit (1) to couple a preparative to a capillary column, to allow variations of different parameters in uninterrupted analysis. The present paper describes the direct qualitative analysis of rums obtained with the new gas chromatographic system where the trap-splitter unit was used to interconnect a preparative to a capillary Golay column.

MATERIALS AND METHODS

The gas chromatographs and auxiliary equipment used in these experiments were described in detail (1). Figure 1 shows a schematic drawing of the chromatographic systems. Figure 2 shows the trap-splitter unit.

The preparative chromatograph was Hewlett Packard[3] 5754B provided

[3] Trade names in this publication are used only to provide specific information. Mention of a trade name does not constitute a warranty of equipment or materials by the Agricultural Experiment Station of the University of Puerto Rico, nor is this mention a statement of preference over other equipment or materials.

with both dual flame ionization detector (FID) and thermal conductivity detector (TCD), a two-pen, two-channel recorder, and a heated backflush valve. The analytical chromatograph was Hewlett Packard 5750B, with dual FID and a two-pen, two channel recorder. The preparative column was a 3 m × 12.7 mm o.d. stainless steel 316 tube filled with acid washed 60/80 mesh, and Chromosorb W coated with 10% Carbowax 20M. The analytical column used was a small bore stainless steel capillary 91 m × 0.25 mm i.d. coated with polyethylene glycol (ucon) 75H 90,000.

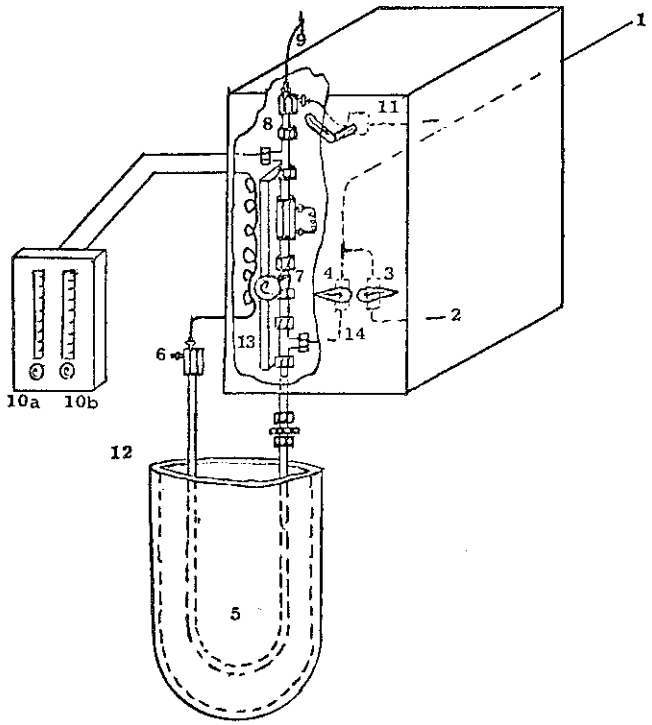

FIG. 2.—Trap splitter apparatus; 1—sample inlet; 2—sample outlet; 3— and 4—shut off valves; 5—U-bent trap in liquid nitrogen bath; 6—exit; 7—expander valve with bellow valve; 8—main capillary carrier entrance; 10—flowmeter; 11—splitter toggle valve; 12—flash heater; 13— and 14—cartridge heater.

The experiments were conducted with a system arranged as in figure 1. An accurate volume of rum (0.8 ml) was introduced in the preparative column by syringe injection. The carrier gas and/or sample emerging from the preparative chromatograph entered in the trap-splitter (figure 2) through inlet 1, and was vented outside when valve 3 was opened and valve 4 closed. Desirable portions of the preparative sample were collected in the trap, previously placed in liquid nitrogen, by simultaneously closing

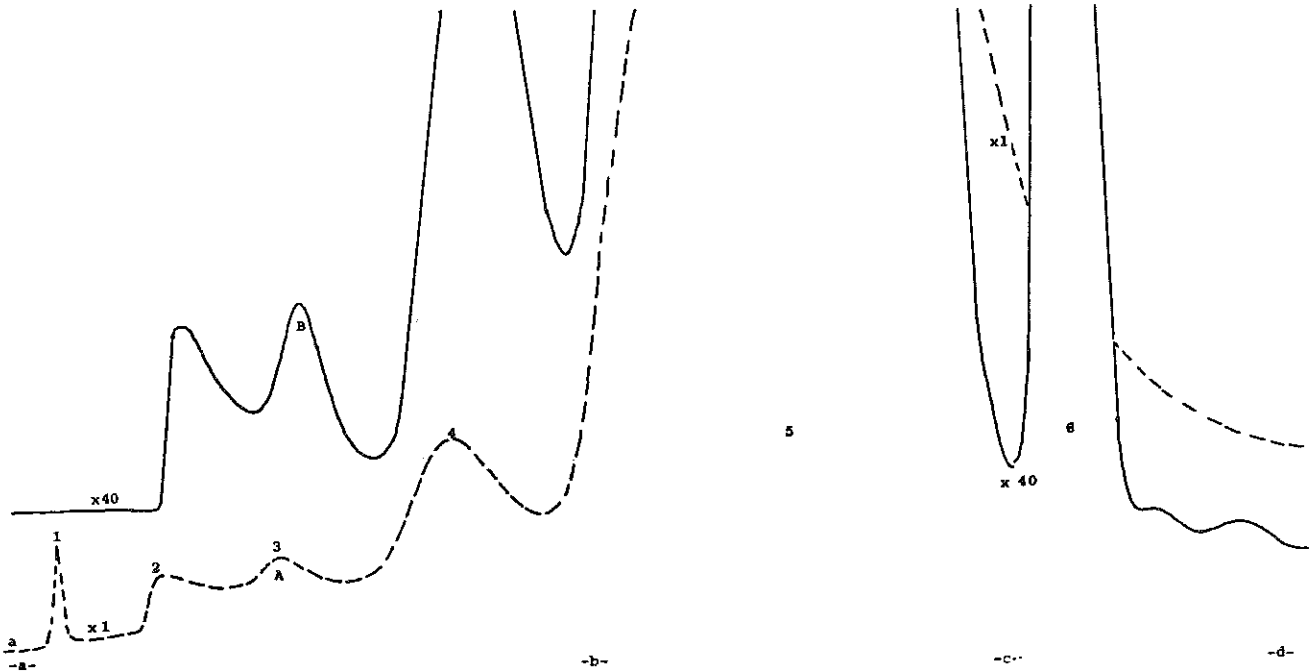

FIG. 3.—Preparative chromatogram of 0.8 ml Puerto Rican Rum R-661. A. Thermal conductivity detector signal; 1—air; 2—acetaldehyde; 3—methyl acetate; 4—ethyl acetate; 5—ethyl alcohol water; 6—isoamyl-alcohol. Over all duration from a to b 35 min., from b to c 1 hr 15 min and c to d 15 min. Recorder speed 6.3 mm/min.

valve 3 and opening valve 4. During this operation trap outlet 6 was kept open and valve 7 closed, while carrier gas was allowed at 6 and through 8 to the capillary column 9 with needle valves 10 open all the way and splitter valve 11 closed. The volatile components separated with Carbowax 20M preparative column were trapped first as a single fraction, until ethyl alcohol began to emerge. In order to stop the collection at this point, valve 4 and exit 6 were closed simultaneously, while valve 3 was opened; the carrier gas from the preparative column was vented outside again through outlet 2. Then, this first fraction collected in the trap was analyzed at the capillary column, while the preparative separation continued uninterrupted. This was accomplished by opening the splitter

TABLE 1.—*Preparative chromatographic conditions for figure 3*

Sample size	0.8 ml
Helium carrier flow	70 ml/min
Helium back flow	130 ml/min
Carrier pressure	2.8 kg/C^2
Oven temperatures:	
Initial	30°C (Oven opened)
During EtOH ejection	60°C
During H_2O ejection	100°C
Final	150°C
TCD temperature	200°C
TCD current	150 ma
FID temperature	240°C
TCD: FID flow ratio	44:1
Injection	5 ml syringe
Injection temperature	200°C
Back flush valve temperature	160°C
Recorded speed	6.3 mm/min

TABLE 2.—*Chromatographic and trap-splitter conditions for capillary separations figures 4–7*

Sample size	2 ml-conc.
Helium carrier flow	1 ml/min
Carrier pressure	1.8 kg/C^2
Helium make-up gas	25 ml/min
Oven temperature	40°C
FID temperature	Trap-splitter
Splitter ratio	1:60
Trap-splitter pressure	1.8 kg/C^2
Trap-splitter column outlet flow	45 ml/min
Trap-splitter temperatures:	
Trap inlet	200°C
Trap	200°C
Expander	200°C
Inlet, outlet valves	120°C
Recorded speed	6.3 mm/min

valve 11 two or three minutes previous to the analysis, while rotameter valve 10a was closed; expander valve 7 was opened; the liquid nitrogen bath was removed and the flash heater 12 was heated to about 200° C for several minutes. Finally, the flow through 10a was restored and valves 7 and 11 were closed again. A high boiling fraction was collected in the same way, after ethyl alcohol and water left the preparative column, and then analyzed with the capillary Golay column.

The volatile and high boiling preparative fractions of three Puerto Rican rums (P-654, R-656 and R-661) and a Jamaican rum (R-677) were analyzed with the trap-splitter following the procedure described above.

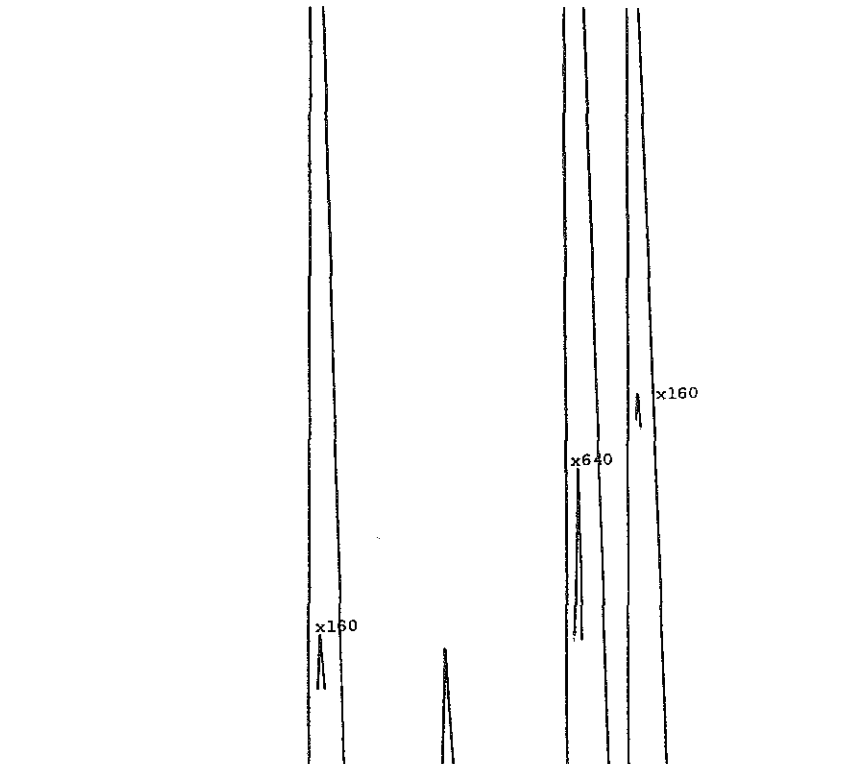

FIG. 4.—Capillary chromatogram of the volatile preparative fraction (a to b) of 2 ml R-654. 1—acetaldehyde; 2—methyl acetate; 3—unknown; 4—ethyl acetate; 5—ethyl alcohol. The remaining signals have not been identified. Recorder speed 6.3 mm/min.

The ucon capillary column was placed in chromatograph (A) followed by the trap-splitter unit (B) and the Carbowax 20M preparative column in position (C). The volatile preparative fraction was trapped according to figure 3, which was taken at conditions given in table 1. The whole portion from A to B was separated at 30° C, trapped and then analyzed at the capillary column with the trap-splitter set at conditions given in

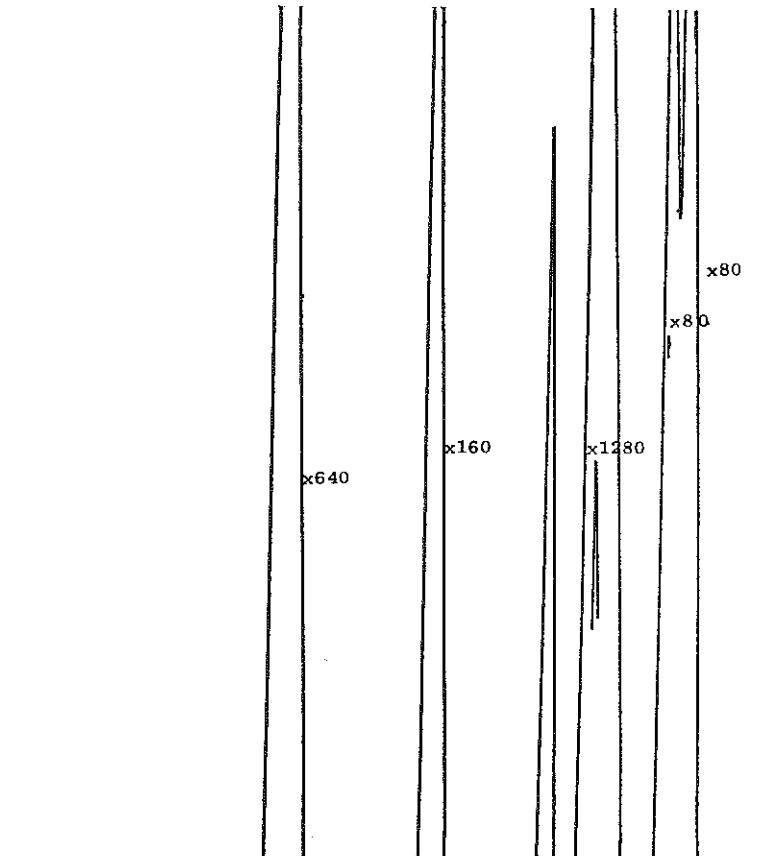

FIG. 5.—Capillary chromatogram of the volatile preparative fraction (a to b) of ml R-656. 1—acetaldehyde; 2—methyl acetate; 3—unknown; 4—ethyl acetate; 5—ethyl alcohol. The remaining signals have not been identified. Recorder speed 6.3 mm/min.

table 2. The capillary separations of this volatile fraction for 2 ml of the three Puerto Rican rums (R-654, 656 and 661) and the Jamaican rum (R-677) are shown in figures 4, 5, 6, and 7, respectively. For the high boiling fraction, 0.8 ml of rum was separated at the preparative column. The separation was allowed to proceed until the top of the isoamyl alcohol signal appeared in the chromatogram at 100° C, in figure 3. At this point collection was started by raising the temperature instantly to 150° C, reversing the carrier flow with the back-flush valve, and finally increasing the carrier back flow rate to 130 ml/min.

The capillary separations corresponding to the high boiling fraction of

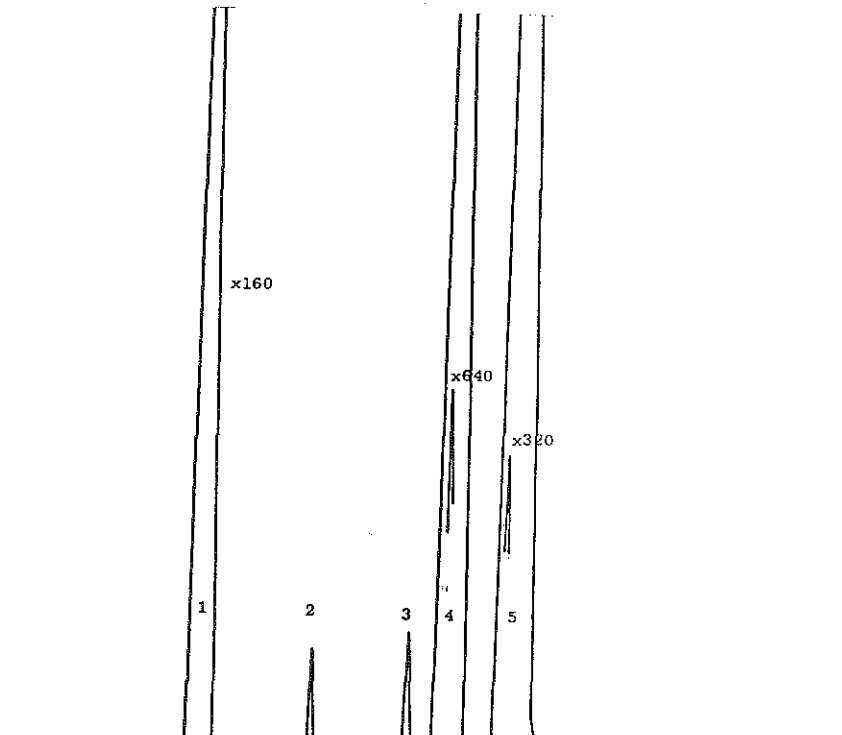

FIG. 6.—Capillary chromatogram of the volatile preparative fraction (a to b) of 2 ml R-661. 1—acetaldehyde; 2—methyl acetate; 3—unknown; 4—ethyl acetate; 5—ethyl alcohol. The remaining signals have not been identified. Recorder speed 6.3 mm/min.

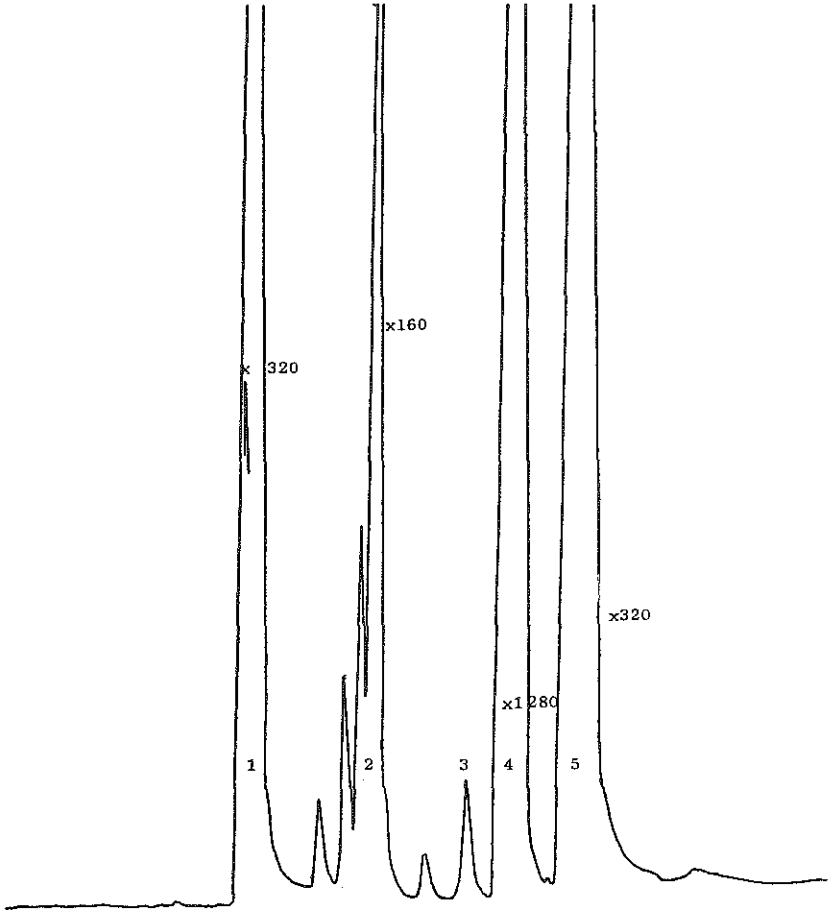

FIG. 7.—Capillary chromatogram of the volatile preparative fraction (a to b) of 2 ml R-677. 1—acetaldehyde; 2—methyl acetate; 3—unknown; 4—ethyl acetate; 5—ethyl alcohol. The remaining signals have not been identified. Recorder speed 6.3 mm/min.

0.8 ml of the four rums, are shown in figures 8 through 11. Conditions are given in table 3.

RESULTS AND DISCUSSIONS

Inspection of the various capillary chromatograms of the preparative volatile fraction, figures 4 through 7, show about 10 congeners with retention times shorter than that of ethyl alcohol. There are four main signals: 1) is acetaldehyde; 2) methyl acetate; 3) ethyl acetate; and 4) ethyl alcohol. Between these main signals appeared a number of unidentified peaks which are more intense in the Jamaican rum than in the Puerto Rican rums included in this investigation. Independent chromato-

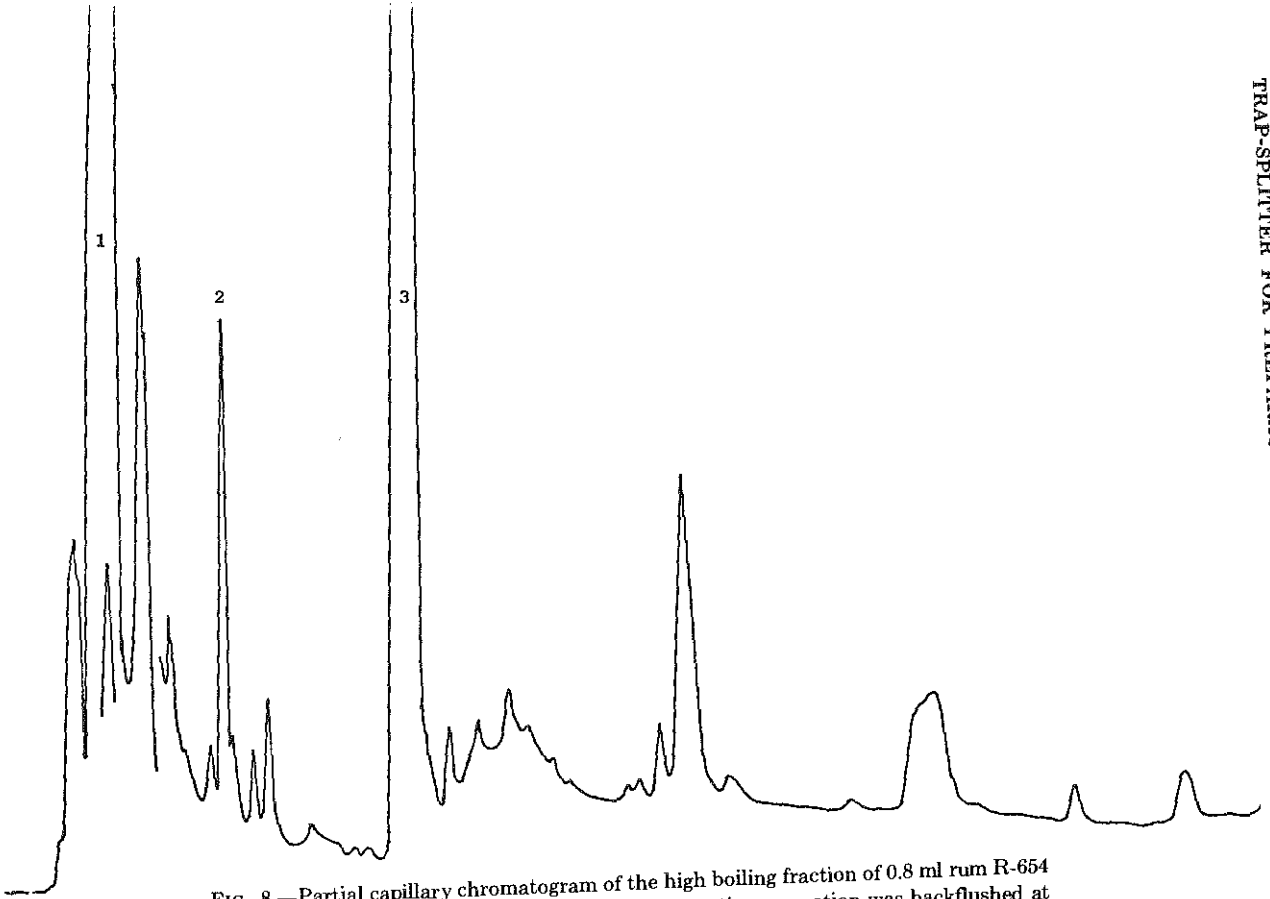

FIG. 8.—Partial capillary chromatogram of the high boiling fraction of 0.8 ml rum R-654 trapped during one hour immediately after the preparative separation was backflushed at the top of isoamyl alcohol. The main signal is isoamyl alcohol, and the remaining are unknown. Approximate retention times: ethyl alcohol 30 min (not shown), isoamyl alcohol, 52 min; signal 2, 56 min; signal 3, 62 min. Recorder speed 6.3 mm/min.

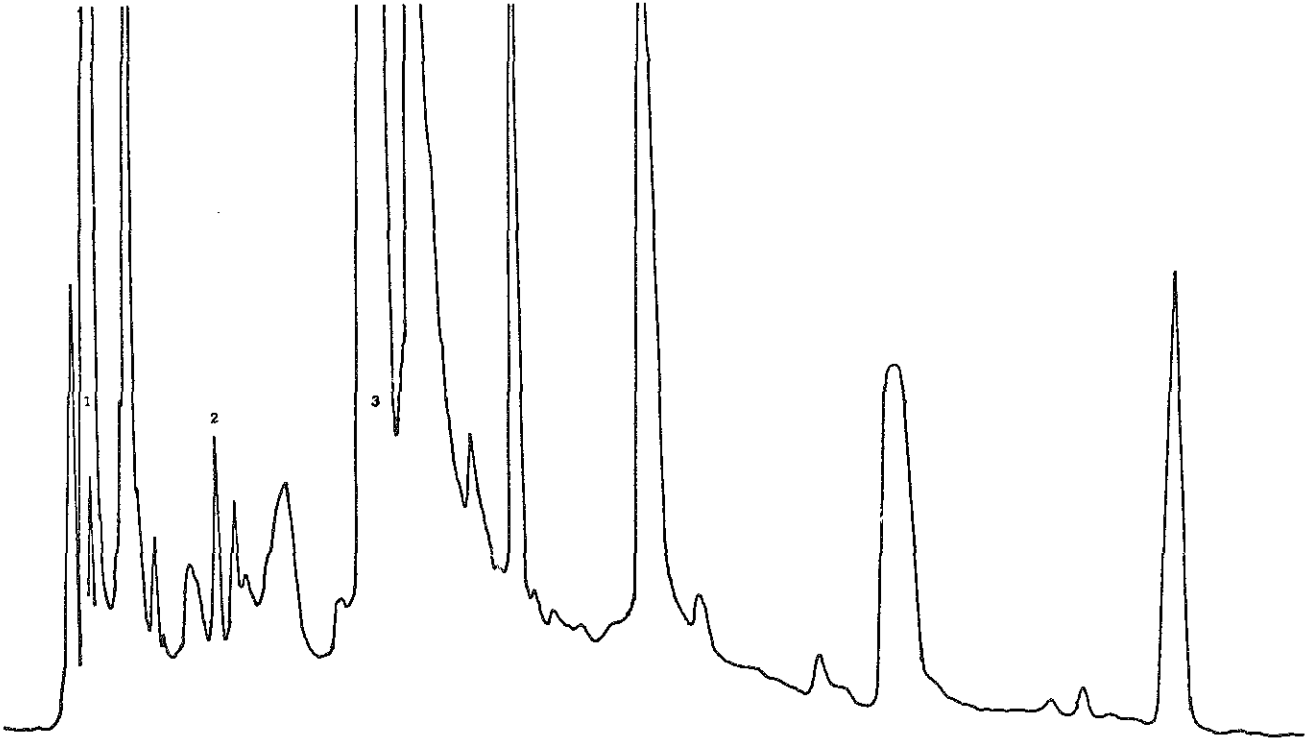

FIG. 9.—Partial capillary chromatogram of the high boiling fraction of 0.8 ml rum R-656 trapped during one hour immediately after preparative separation was backflushed at the top of isoamyl alcohol. The main signal is isoamyl alcohol, and the remaining are unknown. Approximate retention times: ethyl alcohol 30 min (not shown); isoamyl alcohol, 52 min; signal 2, 56 min; signal 3, 62 min. Recorder speed 6.3 mm/min.

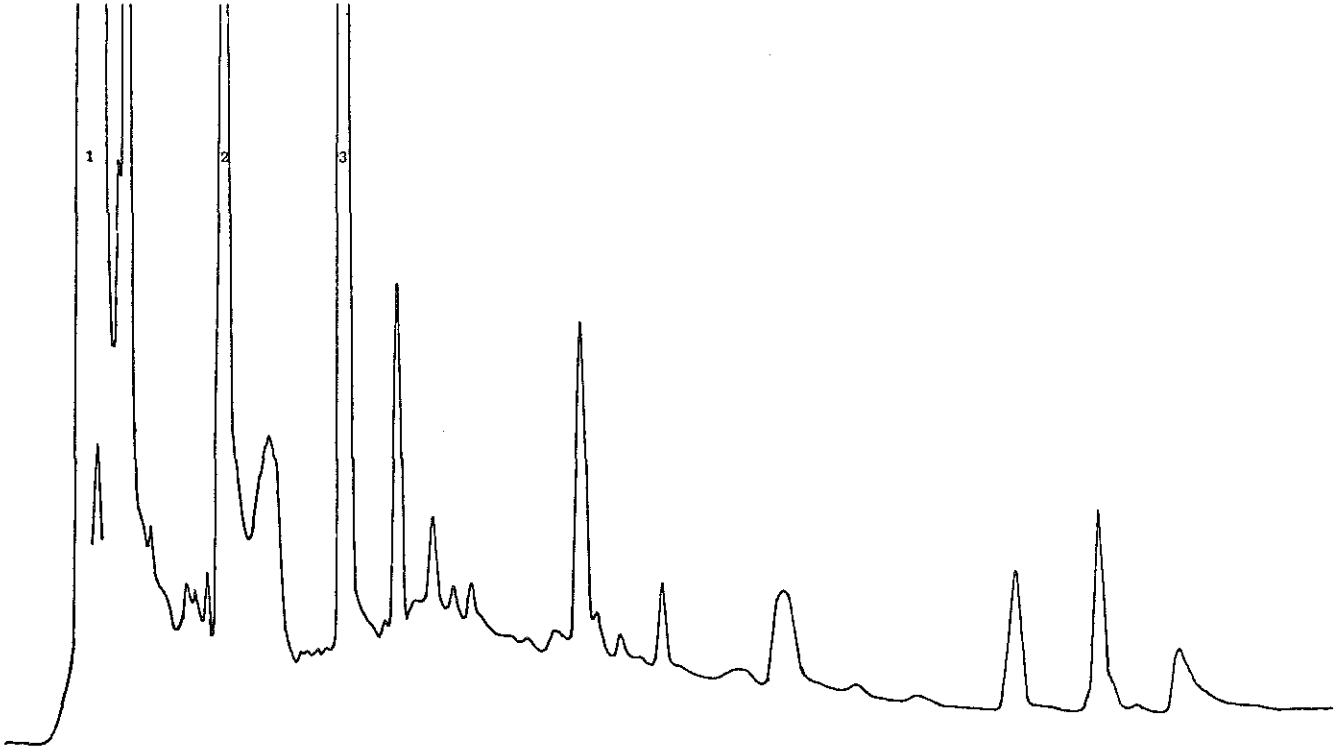

FIG. 10.—Partial capillary chromatogram of the high boiling fraction of 0.8 ml rum R-661 trapped during one hour immediately after the preparative separation was backflushed at the top of isoamyl alcohol. The main signal is isoamyl alcohol, and the remaining are unknown. Approximate retention times: ethyl alcohol 30 min (not shown); isoamyl alcohol, 52 min; signal 2, 56 min; signal 3, 62 min. Recorder speed 6.3 mm/min.

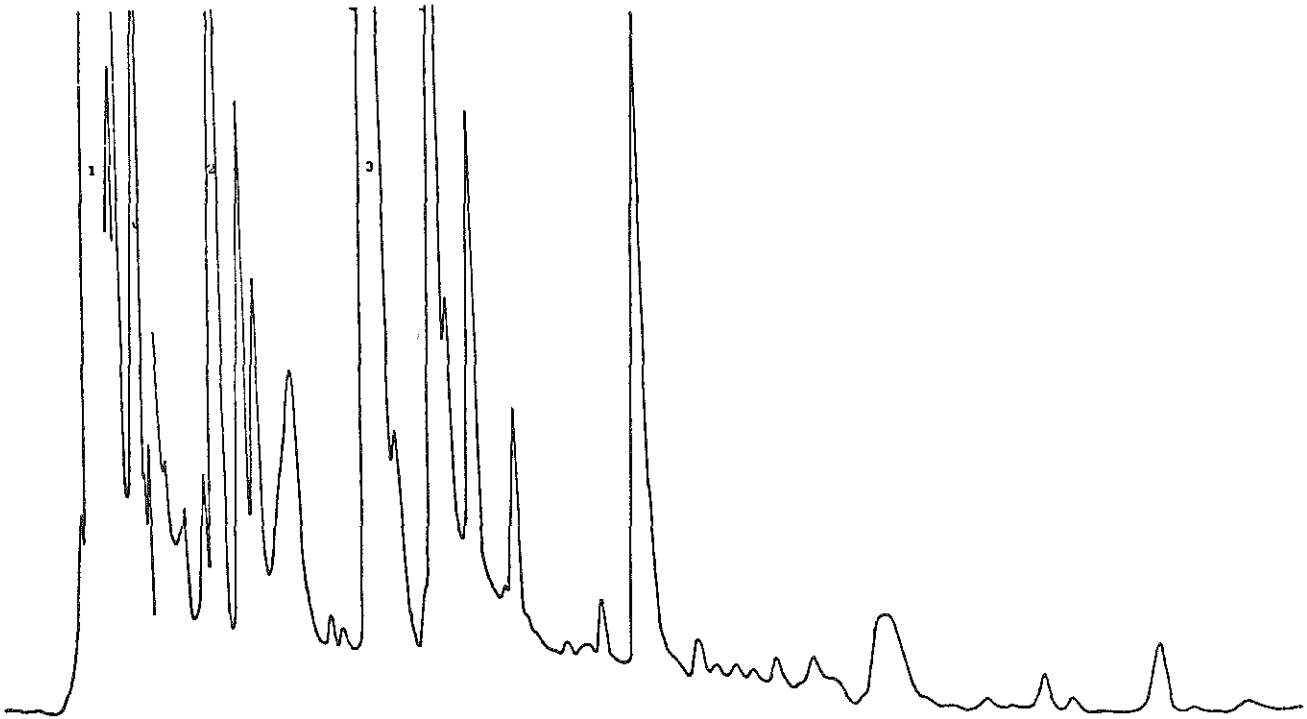

FIG. 11.—Partial capillary chromatogram of the high boiling fraction of 0.8 ml rum R-677 trapped during one hour immediately after the preparative separation was backflushed at the top of isoamyl alcohol. The main signal is isoamyl alcohol, and the remaining are unknown. Approximate retention times: ethyl alcohol 30 min (not shown); isoamyl alcohol, 52 min; signal 2, 56 min; signal 3, 62 min. Recorder speed 6.3 mm/min.

TABLE 3.—*Chromatographic and trap-splitter conditions for capillary separation figures 8–11*

Sample size	0.8 ml-conc.
Helium carrier flow	0.67 ml/min
Carrierr pressure	1.4 kg/C^2
Oven temperatures:	
Initial	30°C/30 min
Final	120°C
Temperature program	10°C min
FID temperature	240°C
Injection	Trap-splitter
Trap-splitter pressure	3.2 kg/C^2
Trap splitter flow	22 ml/min
Trap-splitter temperatures:	
Trap inlet	210°C
Trap	230°C/6 min
Expander	210°C
Inlet, outlet valves	130°C
Recorder speed	6.3 mm/min

graphic separations of congeners belonging to the high boiling fraction of rum taken with the same columns and trap-splitter arrangement, also proved to be high efficient, in this case starting from isoamyl alcohol, figures 8 through 11. The capillary chromatograms are well resolved, revealing high concentrations of some new components. More than fifty signals appeared in this region of the chromatogram, with quite large variations in the composition of the rums.

Although trapping of congeners belonging to the ethyl alcohol and water region was not possible with the preparative column used, the method is a tremendous improvement over the regular direct analytical methods and other separations which employ pre-concentration techniques, as solvent-solvent extraction and distillation, which invariably introduce contamination in the sample analyzed. The method described is highly sensitive and discriminates more readily among samples than regular high efficiency gas chromatography with packed columns.

RESUMEN

Varios rones comerciales de Puerto Rico y uno de Jamaica se analizaron usando una trampa-divisor desarrollada y probada en la Planta Piloto de Ron con el fin de efecturar un acoplamiento efectivo de columnas capilares y columnas preparatorias, de manera que esas dos técnicas cromatográficas sean combinadas para el análisis directo de bebidas alcohólicas. Los análisis fueron efectuados utilizando la trampa-divisor colocada en el centro de un sistema de dos columnas. A la entrada se conecta una columna preparatoria de 3 mm × 12.7 mm de

diámetro externo rellenada con 10% Carbowax 20M en Chromosorb W, 60/80, lavado con ácido, y a la salida se acopla la columna capilar de 91 m × 0.25 mm impregnada con ucon 75H 90,000. La columna preparatoria colocada en un cromatógrafo diferente al de la columna capilar concentra los componentes volátiles de los rones que eluyen antes del alcohol etílico. Independientemente se obtienen con la misma columna concentrados de componentes pesados que eluyen después de alcohol isoamílico. Después de ser retenidas en la trampa-divisor, los subsiguientes análisis capilares independientes de las dos fracciones demostraron que en los rones investigados hay unos 10 componentes antes de la señal de alcohol etílico y alrededor de 50 componentes después de la señal de alcohol isoamílico.

LITERATURE CITED

1. Batiz, H. and Rosado, E., 1977. A Trap-Splitter Unit for Coupling Preparative Gas Chromatographic Columns to Analytical Columns, J. Agri. Univ. P.R. 61(1): 108–112.
2. Batiz, H. and Soltero, E., 1976. Preparative-Capillary Gas Chromatographic Systems for Trace Analysis of Rum, J. Agri. Univ. P.R., 60(4): 559–584.
3. Bayer, E., 1966. Quality and Flavor by Gas Chromatography, J. Gas Chrom. 4: 669–73.
4. García-Morín, M., Aguilera, C., and Sánchez de Torres, C., 1965. Analysis of Puerto Rican Rums by Gas Chromatography, Proc. XII Congr. I.S.S.C.T. Elsevier Publishing Co., Amsterdam, Holland.
5. Hashimoto, N. and Kuroiwa, L., 1966. Gas Chromatographic Studies on Volatile Alcohols and Esters of Beer, J. Inst. Brew. 72: 151–162.
6. Kahn, J. H., La Roe, E. G., and Conner, H. H., 1968. Whiskey Composition Identification of Components by Single-Pass Gas Chromatography, Mass-Spectrometry, J. Food Sci. 33: 395–9.
7. Kahn, J. H., Shipley, P. A., La Roe, E. G., and Conner, H. A., 1969. Whiskey Composition: Identification of Additional Components by Gas Chromatography-Mass Spectrometry, J. Food Sci. 34: 587–91.
8. Liebich, H. M., Koening, W. A., and Bayer, E., 1970. The Analysis of the Flavor of Rum by Gas-Liquid Chromatography and Mass Spectrometry, J. Chrom. Sci. 8: 527–33.
9. Maarse, H. and ten Noever de Brauw, M. C., 1966. The Analysis of Volatile Components of Jamaican Rum, J. Food Sci. 3: 951–5.
10. Schaefer, J. and Timmer, R., 1970. Flavor Components in Cognac, J. Food Sci. 35: 10–12.
11. Williams, A. A. and Tucnott, O. G., 1972. The Volatile Components of Scotch Whiskey, J. Sci. Food Agri. 23: 1–7.