Methanol Analysis by Gas Chromatography—Comparative Study Using Three Different Columns[1]

Guillermo Martínez-Segura, Marta I. Rivera and Luis A. García[2]

ABSTRACT

The methanol analysis in ethanol 80° P was performed efficiently by gas chromatography. Best results were obtained with a column packed with Carbowax 20M on Carbopack BAW or THEED on Chromosorb. In both cases a linear response was obtained in a wide range. When samples of unknown composition are analyzed, more than one column must be used to corroborate results, avoiding the possibility of false identification because of superimposition of signals.

INTRODUCTION

Methyl alcohol is a toxic compound whose products of oxidation upon absorption by the body cause degeneration of the reception cells of the retina, the optic disk and nerve. The intoxication is followed by headache, nausea, vomiting and abdominal pain (15). But Kissin and Begleiter postulate that low concentrations of methanol in ethanol do not pose significant physiological hazard (6).

The determination of methanol in distilled alcoholic beverages has been a recurrent subject of research, because the small amounts present make it very difficult to detect. The Chromotropic Acid Colorimetric method, the method currently accepted by AOAC (14), depends on the maintenance of rigorously controlled conditions to obtain reproducible results (1, 4, 12, 13). The presence of lignin, glucose and glucose oligomers interfere with the assay, causing overestimation of concentrations (5). Acid purification prior to the analysis is mandatory because decomposition of chromotropic acid affects methanol determination; this method normally takes around 4 hours (11).

Gabri and Salvagiotto (3) described a gas chromatographic method based on a glass column packed with Carbopack C, which was good for methanol concentrations greater than 400 mg/100 ml ethanol solution. Martin et al. (10) determined methanol by gas chromatography working with two 28-ft-long columns in series (20% Carbowax 20M on Gas Chrom P and 5% Carbowax 20M on Haloport F). DiCorcia et al. (2) obtained excellent separations at p/m range of methanol in ethanol solutions, when using Carbopack B modified with 3% PEG 20M + 2.4% trimesic

[1] Manuscript submitted to Editorial Board on March 29, 1984.

[2] Assistant Chemist, Research Assistant, and Laboratory Technician, respectively, Agricultural Experiment Station, Mayagüez Campus, University of P. R.

acid as stationary phase. Martin et al. (9) showed that Carbopack B with 5% Carbowax 20M as stationary phase gave good resolution when using gas-liquid chromatography coupled to mass spectrometry (GC-MS).

This paper describes a single procedure for separating and measuring methanol at the p/m range in alcoholic solutions, by means of a packing of Carbopack BAW with 5% Carbowax 20M. Common congeners present in alcoholic beverages do not interfere with the analysis. A comparative study with two additional columns was done, which suggests that better identification and determination of the compounds can be made if more than one column is used for the analysis.

MATERIALS AND METHODS

The standard procedure for rum congener analysis at the Rum Pilot Plant is performed by gas chromatography in a column packed with Carbowax 20M on Chromosorb WAW (8), with a Hewlett-Packard[3] instrument, model 5750, equipped with a flame ionization detector and a Hewlett-Packard model 3390A integrator. Three analytical columns were evaluated, two of them (A and B) were packed in our laboratory. Before packing, the tubing was cleaned in succession with nitric acid, water, chloroform, acetone, carbon tetrachloride, and methylene chloride, then dried at 150° C with a small flow of helium. The columns were conditioned for 24 hours with a 20-30 ml/min helium flow at 100°C, before the analysis. Column C was obtained from Supelco (Bellefonte, PA).

Column A (PPR 159)—A stainless steel tubing 18 ft × ⅛ in O.D. packed with 5% Carbowax 20M/Chromosorb WAW (60/80 mesh).

Column B (PPR 160)—A stainless steel tubing 10 ft × ⅛ in O.D. packed with 15% THEED (tetrahydroxyethylenediamine)/Chromosorb WAW (100/120 mesh).

Column C (PPR 161)—A glass tubing 6 ft × ¼ in O.D. packed with 5% Carbowax 20M/Carbopack BAW (80/120 mesh).

Several settings were tested for the three columns. Table 1 shows the experimental conditions giving optimal results.

All of the solutions were prepared in our laboratory with ethanol 80° P as solvent obtained by mixing redistilled neutral alcohol and deionized distilled water. The calibration curves were prepared with ACS grade methanol in a range between 0.79 and 79.15 mg/100 ml.

Table 2 presents the composition of a standard solution (P-50) which includes common compounds (congeners) present in an alcoholic beverage.

[3] Trade names 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.

TABLE 1.—*Optimal chromatographic conditions for methanol analysis in three different columns*

Condition	Column		
	A	B	C
Carrier pressure (lb/in^2)	40	40	40
Helium flow (ml/min)	20	20	10
Air flow (ml/min)	300	350	295
Hydrogen flow (ml/min)	35	30	55
Post Inj. interval (min)	4	10	0
Lower temp. (°C)	50	65	58
Upscale programming rate (°C/min)	10	4	6
Upper temp. (°C)	160	85	160
Injection port temp. (°C)	150	150	115
FID temperature (°C)	200	200	230
Attenuation	200	10	200

TABLE 2.—*Composition of the standard solution P-50*

No.[1]	Composition	mg/100 ml
1	Acetaldehyde	22.8
2	Methanol	8.0
3	Methyl acetate	7.5
4	Ethyl alcohol	solvent
5	Isopropyl alcohol	5.3
6	Ethyl acetate	9.0
7	n-Propyl alcohol	14.5
8	Isobutyl alcohol	6.4
9	n-Butyl alcohol	3.2
10	Acetal	9.2
11	Acetic acid	5.3
12	2-Methyl-1-butanol	3.5
13	3-Methyl-1-butanol	16.0
14	n-Amyl alcohol	4.9
15	Isoamyl acetate	3.4

[1] These numbers are used in the chromatograms for identification purpose.

RESULTS AND DISCUSSION

Using Column A, mixtures of methanol in ethanol 80° P gave two signals when the former was present in higher concentrations than 190 mg/100 ml (fig. 1-A), but only one signal otherwise. When P-50 was analyzed, it was found that acetal had a retention time similar to that of methanol, making their separation and determination difficult. Isopropyl alcohol also eluted simultaneously with ethanol (fig. 1-B and 1-C).

Methanol-ethanol solutions were well resolved in Column B and maintained a linear response in a broad range (fig. 2), but in the analysis of the standard solution P-50, ethyl acetate and acetal eluted at the same

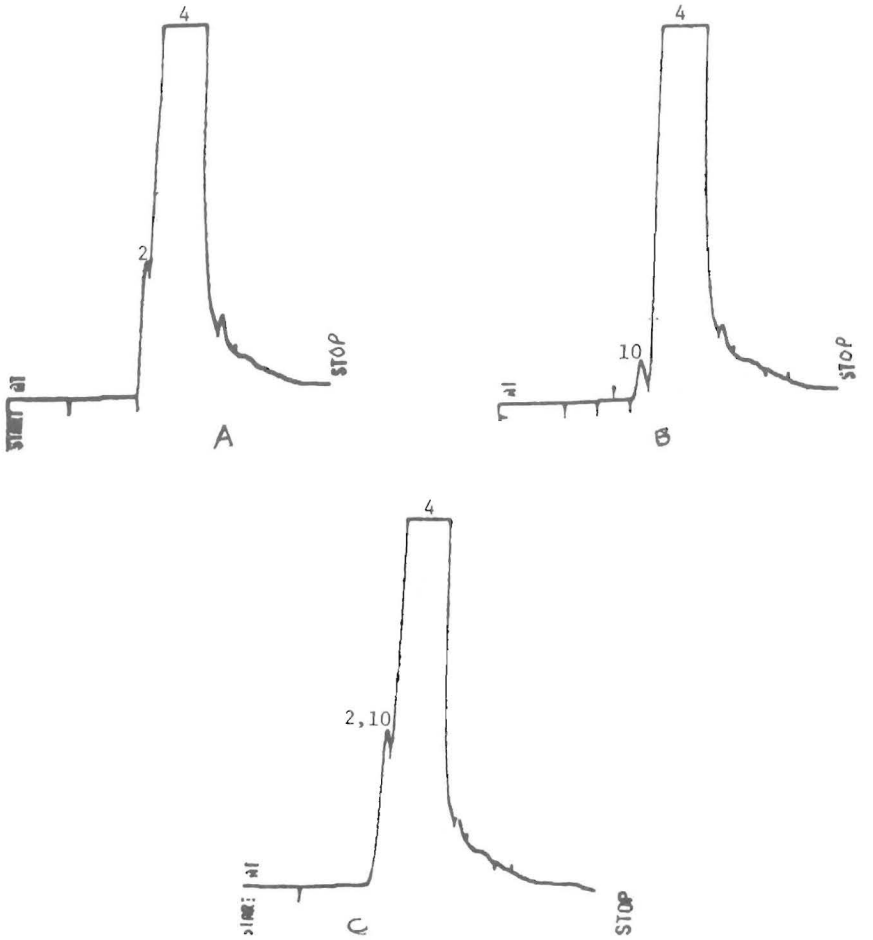


FIG. 1A.—Determination of methanol in ethanol 80° P using column A. B.—Determination of acetal in ethanol 80° P using column A. C.—Analysis of a mixture of methanol and acetal in ethanol 80° P using column A.

retention time. Isopropyl alcohol, a minor congener, if present, eluted at the same retention time of methanol, thus, masking the response (fig. 3-A).

The best results for the analysis of methanol-ethanol solutions were obtained with Column C in terms of resolution (fig. 3-B), sensitivity (1 mg/100 ml), and linearity of response (fig. 4). The analysis of the standard solution presented no interference between the components with the exception of methyl acetate, which eluted simultaneously with ethanol

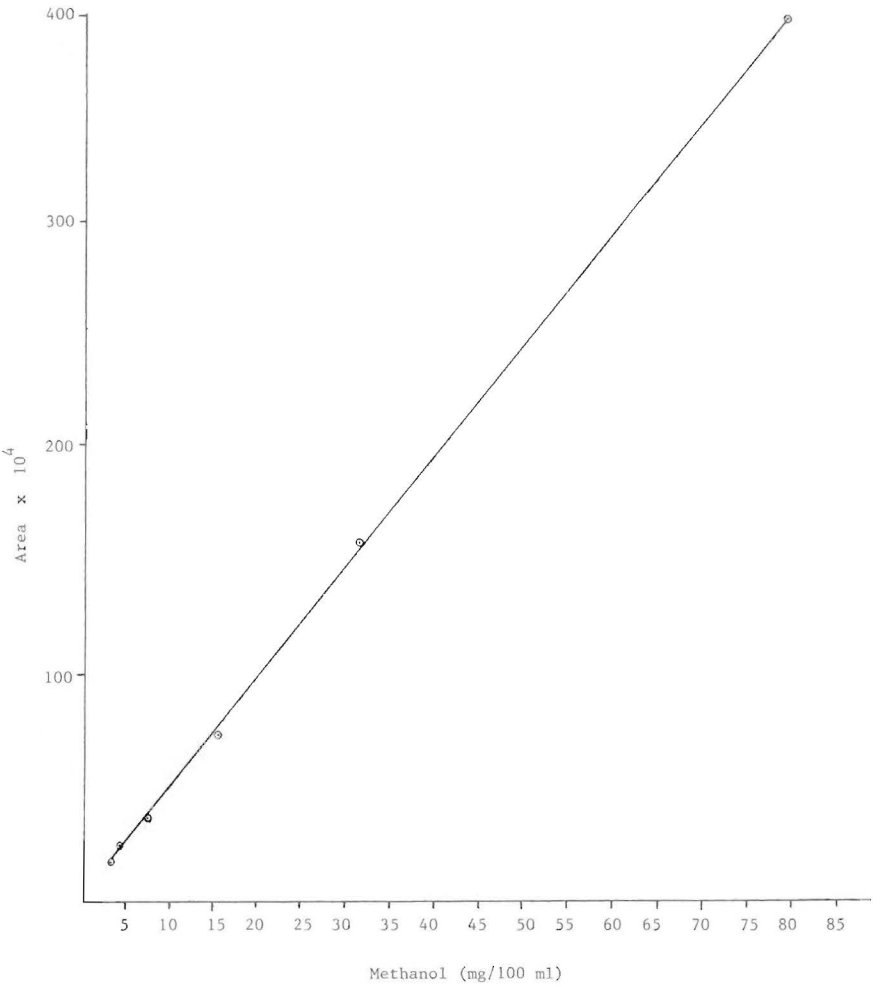


FIG. 2.—Calibration curve of methanol in ethanol 80° P using column B.

(fig. 5). Methyl acetate gave a well defined signal without interferences from known congeners, when using Columns A or B.

The presence of acetic acid in these three columns gave very different results: in Column A it showed no linear response (fig. 6-a and b) and at less than 1.0 g/100 ml it was not detected; in Column B it chemically attacked the stationary phase, and dissolved the THEED from the support thus destroying the column. In column C it had a very good response (fig. 5) at a concentration of 5.3 mg/100 ml.

If an alcoholic beverage (like rum) is going to be analyzed, the possible presence of acetic acid excludes the use of column B. The best determination of common congeners present in an alcoholic beverage was obtained with column C and corroborating results with column A or vice versa. Superimposed signals in one column are well defined in the other, thus eliminating the probability of false identification.

RESUMEN

El metanol en soluciones alcohólicas se analizó por cromotografía de gas en tres tipos diferentes de empaque. Con 5% Carbowax 20M/

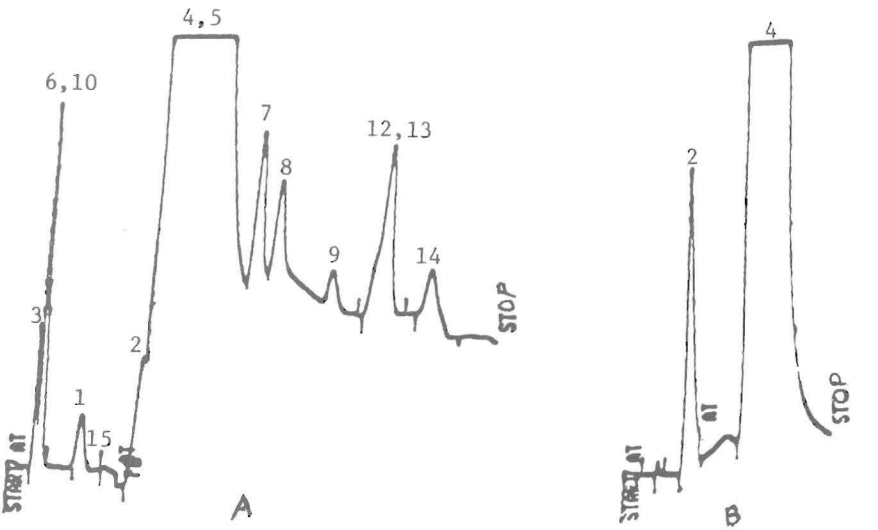


FIG. 3-A.—Analysis of the standard solution P-50 using column B. B.—Determination of methanol in ethanol 80° P using column C.

Carbopack BAW (C) hay excelente sensitividad y resolución. Al usar 15% THEED/Chromosorb WAW (B) hay buena sensitividad pero el alcohol isopropílico presente interfiere con la determinación de metanol. Cuando el empaque es 5% Carbowax 20M/Chromosorb WAW (A) el metanol da señal a concentraciones desde 190 mg/100 ml; sin embargo, si el acetal se encuentra presente no hay resolución. Cuando se usan los dos primeros tipos de empaque se obtiene muy buena linearidad en la respuesta.

La columna C da muy buenos resultados para una muestra con ácido acético; si se usa la columna A no hay linearidad en la respuesta y el ácido acético solamente se detecta a concentraciones mayores de 1.0 g/100 ml. Debe evitarse usar la columna B para analizar ácido acético porque este ácido ataca químicamente el empaque y disuelve la fase estacionaria.

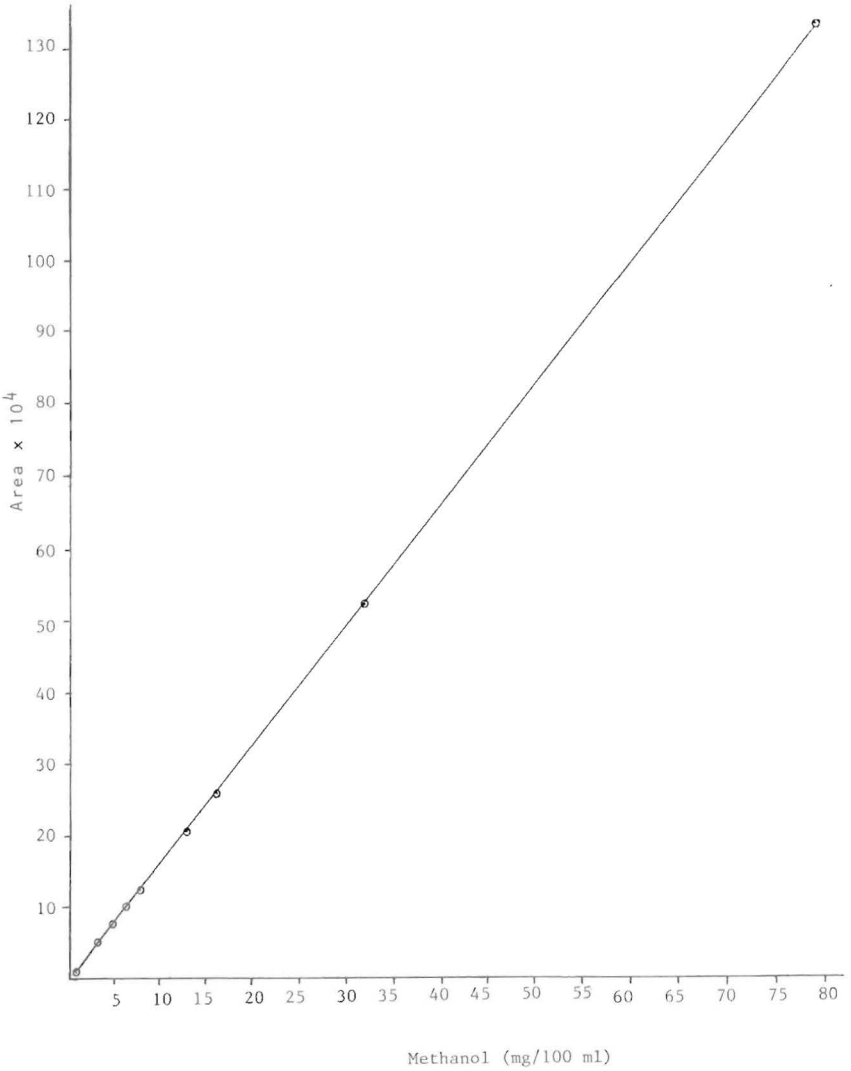


FIG. 4.—Calibration curve of methanol in ethanol 80° P using column C.

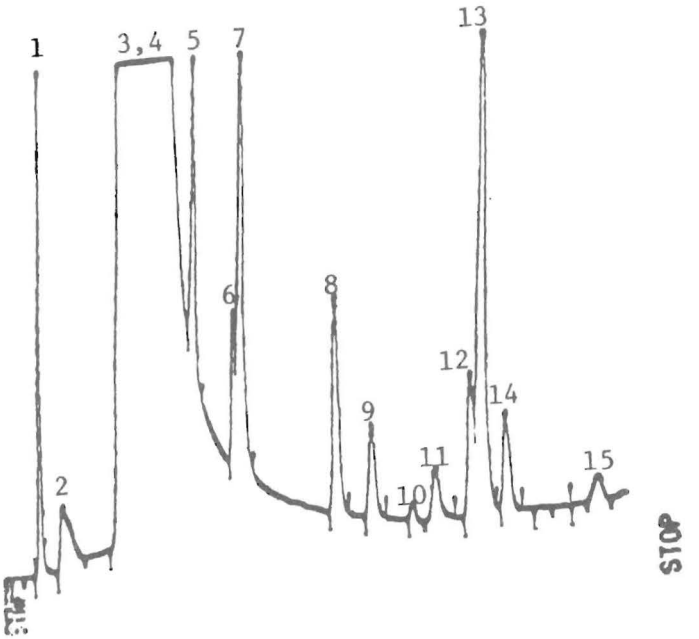
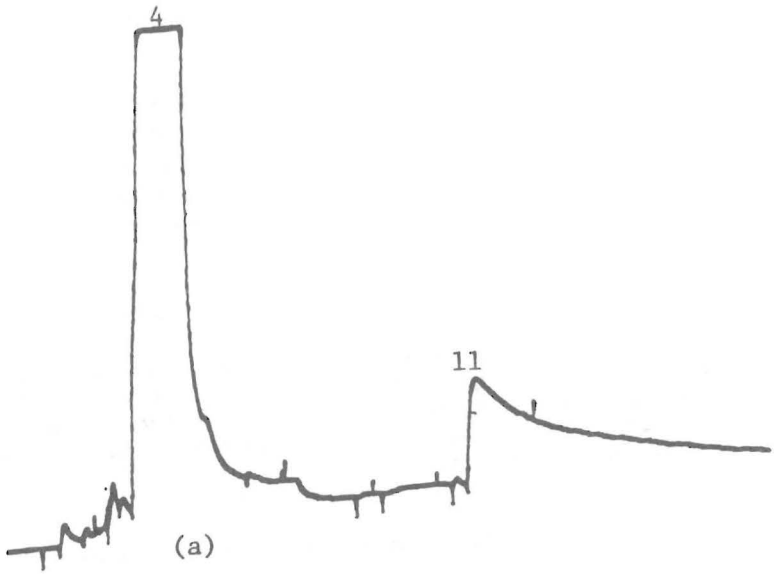


FIG. 5.—Analysis of the standard solution P-50 using column C.



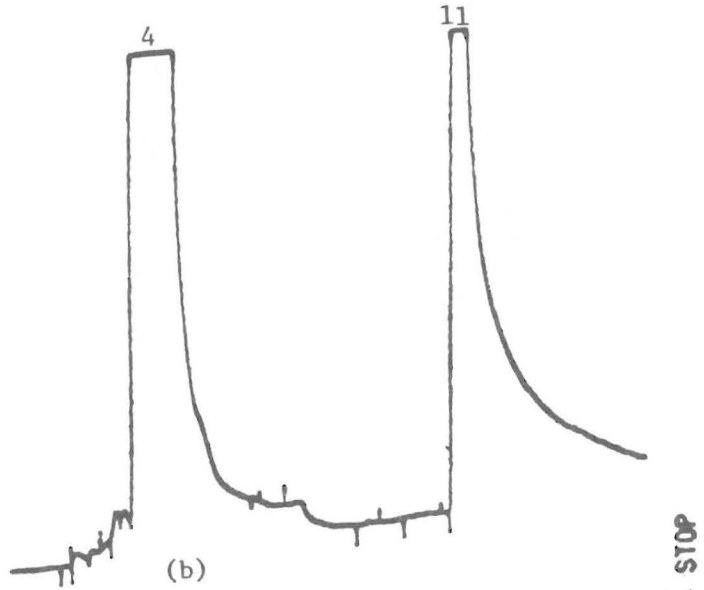


FIG. 6.—Determination of acetic acid in ethanol 80° P using column A. (a) 1.049 g/100 ml; (b) 2.098 g/100 ml.

El análisis de una bebida alcohólica da mejores resultados con las columnas C y A. De esta manera, la segunda corrobora los resultados de la primera. Además, se elimina la falsa determinación de los componentes causada por la superposición de señales. En general, y por las razones expuestas, el análisis por cromatografía de gas de una solución desconocida debe hacerse con dos o más tipos diferentes de empaque.

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