# GAS-CHROMATOGRAPHIC ANALYSIS OF SOME VOLATILE CONGENERS IN DIFFERENT TYPES OF STRONG ALCOHOLIC FRUIT SPIRITS


Vesna Kostik[1*], Shaban Memeti[1], Biljana Bauer[2]

[1*]Institute of Public Health of Republic of Macedonia

[2]Institute of Pharmacognosy, Faculty of Pharmacy, Ss. Cyril and Methodius University



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## ✓ Introduction

Although the major physiologically active component of the most alcoholic beverages is ethyl alcohol, there is a remaining fraction of compounds called congeners. Congeners may be highly volatile compounds, like:

- alcohols,
- acids,
- aldehydes,
- ketones and esters,

which play an important and often unnoticed role in the social use and of the alcohol abuse.

✓ While thousands of different volatile congeners may be found in various drinks at one time or another, several of them have been found to be constantly present as: methyl alcohol, acetaldehyde, ethyl acetate, ethyl formate and the small aliphatic alcohols (*n*–propyl alcohol, isobutyl alcohol, *n*–butanol). They have significant impact on the quality and flavour of alcoholic beverages.

## ✓ Objective of the study

Macedonia has and old and rich tradition in fruit growing and production of distilled beverages. The national brands of distilled spirits are: Rakia which is produced from grapes or grape pomace and plum brandy which is produced from plum.

Aim of our study was to identify and quantitatively analyze alcohol volatile congeners in different types of spirits from the domestic producers in order to evaluate their quality.

## ✓ Samples and analytes

Within the period from 2009 to 2013, a total of hundred samples of three types of grape brandies (lozova rakia, komova rakia and vinjak) and thirty samples of plum brandies (slivova rakia) were tested on the content on several volatile congeners as: methanol, ethyl acetate, 1-propanol (*n*-propanol), 2-propanol (*i*-propanol), 1-butanol (*n*-butanol), *i*-butanol (2-methylpropan-1-ol), *n*-amyl alcohol (*n*-pentanol) and *i*-amyl alcohol (3-methyl-1-butanol). The samples were provided by seven producers located in Macedonia.

## ✓ Methods

The major volatile components in spirits were analyzed using gas chromatography (GC) with a flame-ionization detector (FID).

### ✓ Table 1 Instrumental conditions

- Column: polar fused silica capillary column (30 m x 0.32 mm id. x 0.25 mm film thickness) coated with bonded; poly(ethylene glycol).

- Carrier gas (nitrogen) flow rate – 1.5 $mL \cdot min^{-1}$
- Split ratio – 1:10
- Injection port – 250 $^{0}C$
- FID – 280 $^{0}C$
- Oven program: 60 $^{0}C$ (5 minutes) increasing for 10 $^{0}C \cdot min^{-1}$. The final oven temperature was maintained at 200 $^{0}C$ (10 minutes).

## ✓ Results

### Determination of ethanol

Ethanol is present in alcoholic beverages as a consequence of the fermentation of carbohydrates with yeast and is responsible for the beverage's body .

In our investigations we found that the amount of ethanol in the samples varied from 37.8% (v/v) for grape brandy vinjak to 50.8% (v/v) for plum brandy (Table 2), which are in compliance with Official Regulation [1].

**Table 2. Concentrations (minimum – maximum) of ethanol in fruit spirits, determined by GC-FID (% v/v; n=number of samples; MV)**

| Type of fruit brandy | Concentration of ethanol (% v/v) |
|---|---|
| Grape brandy lozova (n=45) | 40.5 – 50.1 (45.8) |
| Grape brandy komova (n=35) | 40.7 – 50.3 (47.8) |
| Grape brandy vinjak (n=20) | 37.8 – 39.2 (38.5) |
| Plum brandy (n=30) | 46.7 – 50.8 (48.3) |

## Determination of methanol

Methanol is a constituent arising from the enzymatic degradation of pectin contained in fruits. Generally, its quantity is related to the amount of pectin present in fruits used for fermentation. The methanol concentration is suitable for proving the authenticity of fruit spirits [2]. When present in higher concentrations, methanol can caused serious health problems.

In our investigated samples (Table 3), the amounts of methanol in the samples (Table 3) varied from 2.24 mg/100 mL a.a. for grape brandy lozova to 1903 mg/100 mL a.a. for plum brandy.

**Table 3. Concentrations (minimum – maximum) of methanol in fruit spirits, determined by GC-FID (mg/100 mL a.a; n=number of samples; MV)**

| | Grape brandy lozova (n=45) | Grape brandy komova (n=35) | Grape brandy (vinjak) (n=20) | Plum Brandy (n=30) |
|---|---|---|---|---|
| Methanol | 2.24 – 1210 (464.7) | 42.6 – 1276 (721) | 45 – 375 (169) | 245 – 1903 (895) |

## Determination of ethyl acetate

Esters are very important compounds due to their particular contribution to flavour and aroma, since they have the lowest organoleptic threshold [3]. The quantity of this compound presented in the final product can vary widely, since it is synthesized from acetic acid and ethanol [4]. High concentrations of ethyl acetate are indicative of prolonged storage of the row material and probable acetic bacteria spoilage.

The mean values of the concentration of ethyl acetate for studied samples (Table 4) ranged from 3.6 mg/100 mL a.a. for grape brandy lozova to 404 mg/100 mL a.a. for plum brandy and are in compliance with literature data [5]

**Table 4. Concentrations (minimum – maximum) of ethyl acetate in fruit spirits, determined by GC-FID (mg/100 mL a.a; n=number of samples; MV)**

| | Grape brandy lozova (n=45 | Grape brandy komova (n=35) | Grape brandy (vinjak) (n=20 | Plum Brandy (n=30) |
|---|---|---|---|---|
| Ethyl acetate | 3.6 – 248.1 (60.3) | 71.8 – 145 (104.4) | 38 – 223.2 (90) | 51 – 404 (132.5) |

## Determination of higher alcohols

Higher alcohols are characteristic components which are metabolised from amino acids by yeasts during alcoholic fermentation of fruits and other raw materials. The amounts of these compounds depend on the quantity of amino acids in fruits. Higher alcohols have a significant impact on the flavour of alcoholic beverages [6, 7], but are also mildly toxic.

The most important higher alcohols of grape and plum brandies were found to be *i*-propanol, *n*-propanol, *i*-butanol, *n*-butanol, *i*-amyl alcohol and *n*-amyl alcohol. Our investigations showed that *i*-amyl alcohol was the most abundant higher alcohol in all tested samples of grape and plum spirits. The highest mean value for *i*-amyl alcohol content was found in grape brandy komova rakia 176.6 mg/100 mL a.a. (Table 5).

**Table 5. Concentrations (minimum – maximum) of *i*-amyl alcohol in fruit spirits, determined by GC-FID (mg/100 mL a.a; n=number of samples; MV)**

| | Grape brandy lozova (n=45 | Grape brandy komova (n=35) | Grape brandy (vinjak) (n=20 | Plum Brandy (n=30) |
|---|---|---|---|---|
| *i*-amyl alcohol | 46.8 – 273.8 (172.7) | 49.4 – 276.3 (176.6) | 114 – 137 (128) | 98.8 – 135.6 (112.8) |

# Comparison of the chromatograms of whiskey and plum brandy

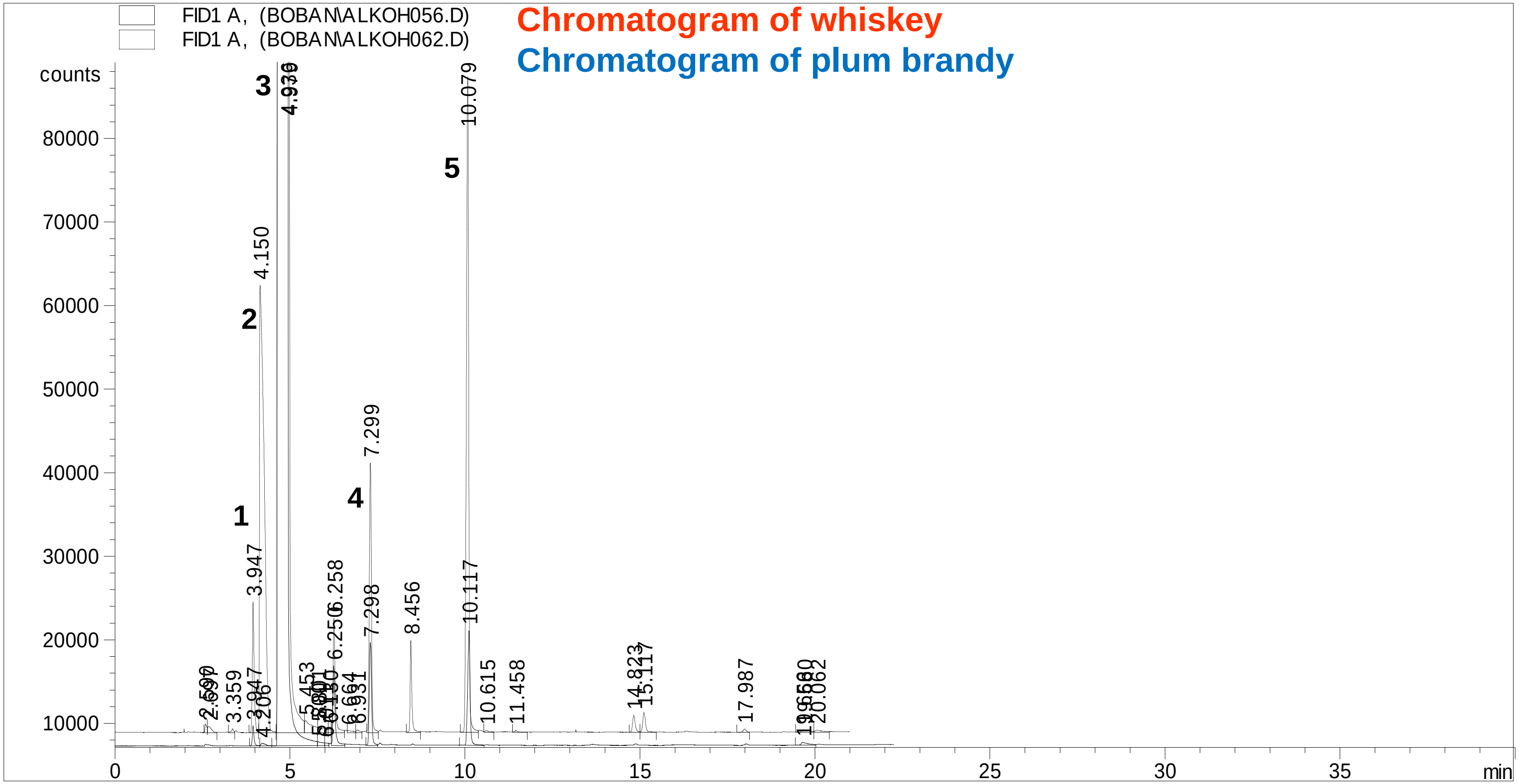


**Figure 1. Chromatograms of whiskey and plum brandy on HP Inowax column: 1. ethyl acetate; 2. methanol; 3. ethanol; 4. *i*-propanol; 5. *i*-amyl alcohol**

# Comparison of the chromatograms of vodka and grape brandy "komova"

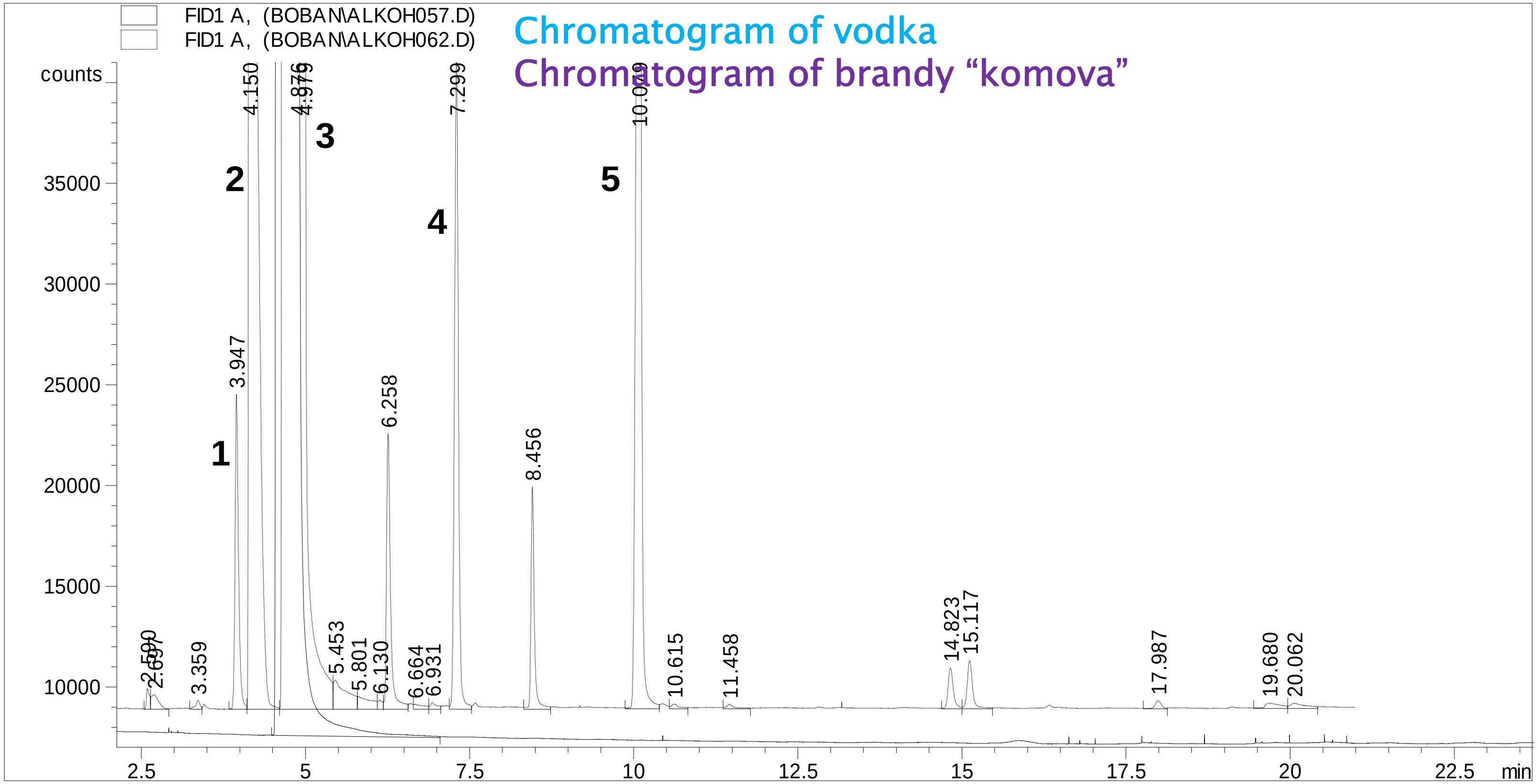


**Figure 2. Chromatograms of vodka and grape brandy "komova" on HP Inowax column: 1. ethyl acetate; 2. methanol; 3. ethanol; 4. *i*-propanol; 5. *i*-amyl alcohol**

## ✓ Conclusions

- The aim of our study was to identify and quantitatively analyze alcohol volatile congeners in different types of spirits from the domestic producers in order to evaluate their quality according to the Official Regulation [1].
- A total of 100 samples of three different types of grape brandies (lozova rakia, komova rakia and vinjak) and 30 samples of plum brandies obtained from seven domestic producers were analyzed on the content of ethanol, ethyl acetate, methanol, *i*–propanol, *n*–propanol, *i*–butanol, *n*–butanol, *i*–amyl alcohol and *n*–amyl alcohol.
- Maximum admissible limits were exceeded for methanol content in twelve of tested samples (2 samples of grape brandy lozova, 3 samples of grape brandy komova, 3 samples of grape brandy vinjak and 4 samples of plum brandies).
- The major higher alcohol present in all tested samples was *i*–amyl alcohol. The content of *i*–amyl alcohol in grape brandy lozova rakia and grape brandy komova rakia didn’t show significant statistical difference, since the row material used was similar between the varieties.

# THANK YOU FOR YOUR ATTENTION