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Evaluating the chemical and metal contamination of commercial Rakı, a grape-based alcoholic beverage from Turkey

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ABSTRACT

Turkish Rakı is one of the most consumed alcoholic beverages in Turkey. The chemical and metal contamination of alcoholic beverages is a threat to human health and lowers the quality of the product. Ethyl carbamate and furfural are carcinogenic to animals, and have been classified as Group 2A and 3 agents respectively by the International Agency for Research on Cancer. Factors, such as raw materials, process time and storage, affect metal concentrations in beverages. Limits for chemicals and metals in Rakı have not yet been established by the Turkish agency. The present study aimed to evaluate the chemical and metal contamination of commercial Turkish Rakı. Thirty-seven different types of Turkish Rakı were purchased from local markets in Turkey. Ethyl carbamate (EC) and furfural (FR) levels were measured by Gas Chromatography-Mass Spectroscopy (GC-MS). Arsenic, copper, lead, and zinc levels were measured by Inductively Coupled Plasma–Optical Emission Spectrometry (ICP-OES). None of the Rakı samples contained EC. Furfural was not detected in commercial Rakı samples but only in illegal Rakı samples. Ethanol and methanol levels complied with Turkish regulation. Our data shows that commercial Rakı from Turkey was contaminated by very low amounts of arsenic (<LOD–0.02 mg/L), copper (0.05–0.41 mg/L), lead (< LOD–0.03 mg/L) and zinc (0.01–0.39 mg/L).

KEYWORDS

Turkish Rakı, ethyl carbamate, furfural, metal contamination, copper

INTRODUCTION

Rakı is a double distilled, traditional aniseed spirit, one of the most consumed alcoholic beverages produced in Turkey (Darici *et al.,* 2019). Rakı was accorded Protected Designation of Origin (PDO) by the Turkish Patent and Trademark Office in 2009 (TPI, 2009). In accordance with this PDO document and the Turkish Food Codex Communiqué on Distilled Alcoholic Beverage (TFC, 2017), Rakı is produced by distilling Suma (grape distillate) with aniseed (only *Pimpinella anisum*) in a traditional copper pot still. Suma is a distillate of grapes/raisins, which are distilled to up to 94.5 % v/v alcohol by column still distillation with the purpose of retaining the flavour and smell of grapes. Rakı is also one of the most adulterated alcoholic beverages in Turkey. It is often mixed with ethyl alcohol, methanol, water, sugar, and aniseed aroma to increase the profit margin. Adulteration with methanol specifically can cause severe health issues, such as blindness, and can even result in death (Ghadirzadeh *et al.,* 2019). In 2020, 33 people lost their lives in Turkey due to consumption of counterfeited Rakı adulterated with methanol. While the addition of methanol to alcoholic beverages can cause many health problems, other types of chemical and metal contamination can be carcinogenic to humans, and their high consumption can cause the same or worse problems as methanol does (Lachenmeier *et al.,* 2011).

Ethyl carbamate (EC) ($C_2H_5OCONH_2$) has been classified by the International Agency for Research on Cancer (IARC) as a Group 2A agent, being carcinogenic to animals and possibly to humans (IARC, 2007). Ethyl carbamate can be formed through multiple pathways, and it forms naturally in fermented products including distilled spirits (Figure 1). The most common pathway for EC formation is the reaction between ethanol and N-carbamyl compounds, such as urea produced from arginine metabolism by yeast or lactic acid bacteria (Choi *et al.,* 2018). EC can also be formed during distillation and 48 hours after the distillation is complete (Bruno *et al.,* 2007). Because of its carcinogenicity, EC has attracted attention in many countries, and its concentrations in alcoholic beverages have been limited (Table 1). However, the Turkish regulatory agency has not yet established the limits for ethyl carbamate, and no data is available for Turkish Rakı. Rakı is one of the most consumed distilled spirits in Turkey and the most prone to adulteration; therefore, the determination of EC levels in Rakı is needed. EC is commonly determined by GC-MS, UPLC-MS and HPLC with a fluorescence detector (Riachi *et al.,* 2014). To our best knowledge, the present study contains the first reported data for EC levels in Rakı.

TABLE 1. Ethyl carbamate limits for alcoholic beverages (µg/kg).

Country	Wine	Distilled spirits	Fruit brandy
Brazil		150	
Canada	30	150	400
France		150	400
United States	15		

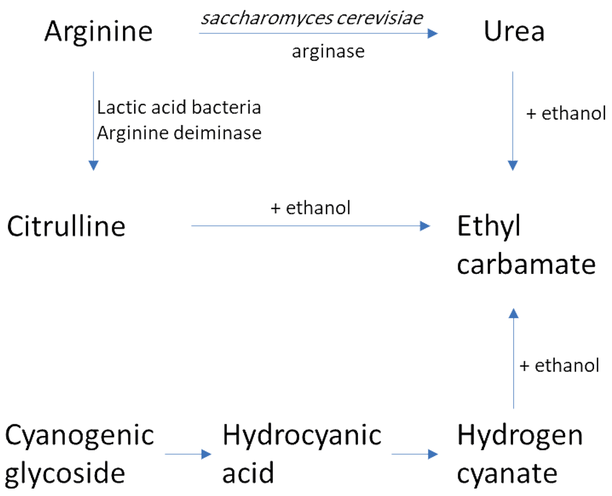

FIGURE 1. Pathways of ethyl carbamate formation in alcoholic beverages (modified from McAdam *et al.*, 2018).

Furfural (FR) (C_4H_3OCHO) is carcinogenic to laboratory animals and has been classified in Group 3 since no data is available for human studies, and not enough tests on animals have been made to be accepted in Group 2A (IARC, 2014). Furfural is a volatile compound toxic to humans and is formed from pentoses in fruits. Alcoholic beverages containing high concentrations of furfural threaten human health; for instance, their consumption may result in pain, diarrhea, headaches and excessive vomiting. Furfural is generally formed when distillation is not carried out properly, especially when applying high heat (Coldea *et al.,* 2014). Homemade alcohols and illegal products can have a high concentration of furfural, because direct high heat is applied, thus producing harmful compounds, a caramel colour and a burnt taste (Coldea *et al.,* 2017). Determination of furfural is generally carried out by using spectroscopy (UV-Vis) and chromatography (GC, GC-MS) techniques (Barbosa-Garcia *et al.,* 2007). Furfural levels in Tequila from Mexico and Pisco from Peru are limited to a maximum of 40 mg/L and 50 mg/L of anhydrous alcohol respectively. The Turkish Food Codex does not limit furfural levels in Rakı; however, it forbids any furfural in the suma. Due to its toxicity, furfural levels in Rakı need to be determined.

The contamination of alcoholic beverages with metals is a threat to human health and can impact the quality of the final product; for example, homemade rum can cause human paralysis because of equipment containing Pb, and metals in alcoholic beverages can cause turbidity, colour change and the formation of congeners (Pohl, 2007; Ibanez *et al.,* 2008). Conversely, alcoholic beverages can be a source of metals beneficial for human health: for example, the consumption of wine can provide many essential minerals, such as Cu, Fe and Zn (Ibanez *et al.,* 2008). Many factors, such as distillation type, raw materials and storage equipment, can affect the levels of metals in the final product (Pohl, 2007). The limits for metal concentrations in alcoholic beverages vary depending on the product; for example, the maximum limit for copper in cachaca from Brazil and Pisco from Peru is 5 mg/L (Menevseoglu, 2019). However, the Turkish Food Codex has not set limits for metal levels in Rakı.

The objective of this study was to evaluate the chemical and metal contamination of commercial Rakı from Turkey. To the best of our knowledge, the data in this study on ethyl carbamate, furfural, and metal concentrations in Turkish Rakı are the first to be reported.

MATERIALS AND METHODS

1. Materials

Commercial Rakı samples (n = 34), and counterfeited Rakı (n = 3) were purchased from local Turkish markets and obtained from manufacturers. Detailed information about the Rakı samples is given in Table 2.

2. Methods

2.1. Determination of ethyl carbamate and furfural by GC-MS

For chemical contamination, a Gas Chromatography Mass Spectroscopy (GC-MS) technique was used following a method modified from Bortoletto and Alcarde (2016). A standard curve for ethyl carbamate (EC) and furfural (FR) was established to quantify the concentration of both these chemicals (Figure 2). Concentrations of 5–350 µg/L EC in 40 % ethanol in water solutions were used. Similarly, to create a standard curve for FR concentrations in Rakı, 1–30 mg furfural/1000 mL in 40 % ethanol in water solutions were used. An Agilent Technologies 7820A GC was used with a 5877B MSD (Santa Clara, CA, USA); this is a single quadrupole mass spectrometry instrument that uses electrospray ionisation to ionise the sample. A DB-WAX UI column (Agilent Technologies, Santa Clara, CA, USA) was used; it was 30 m long and 0.250 mm wide with an inner diameter of 0.25 µm. The initial oven temperature was set at 90 °C for 2 min, increased at a rate of 10 °C/min to 150°C at which it was held for 6 min, and then increased at a rate of 40 °C/min to a final temperature of 230 °C with 2 min of hold time. The injection volume for the analysis was 2 µL. The injection method was a split (20:1) method with an injection port temperature of 220 °C. The pressure of the injection port was set at 8.743 psi. The mass spectrometer source temperature was set at 240 °C and the quadrupole temperature set at 180 °C. The electron energy of the MS was set at 70 eV, and the acquisition type was set to SIM and SCAN mode. For EC and FR, 62 m/z and 95 m/z ions respectively were measured and used for quantification. The validation parameters for EC and FR are given in Table 3.

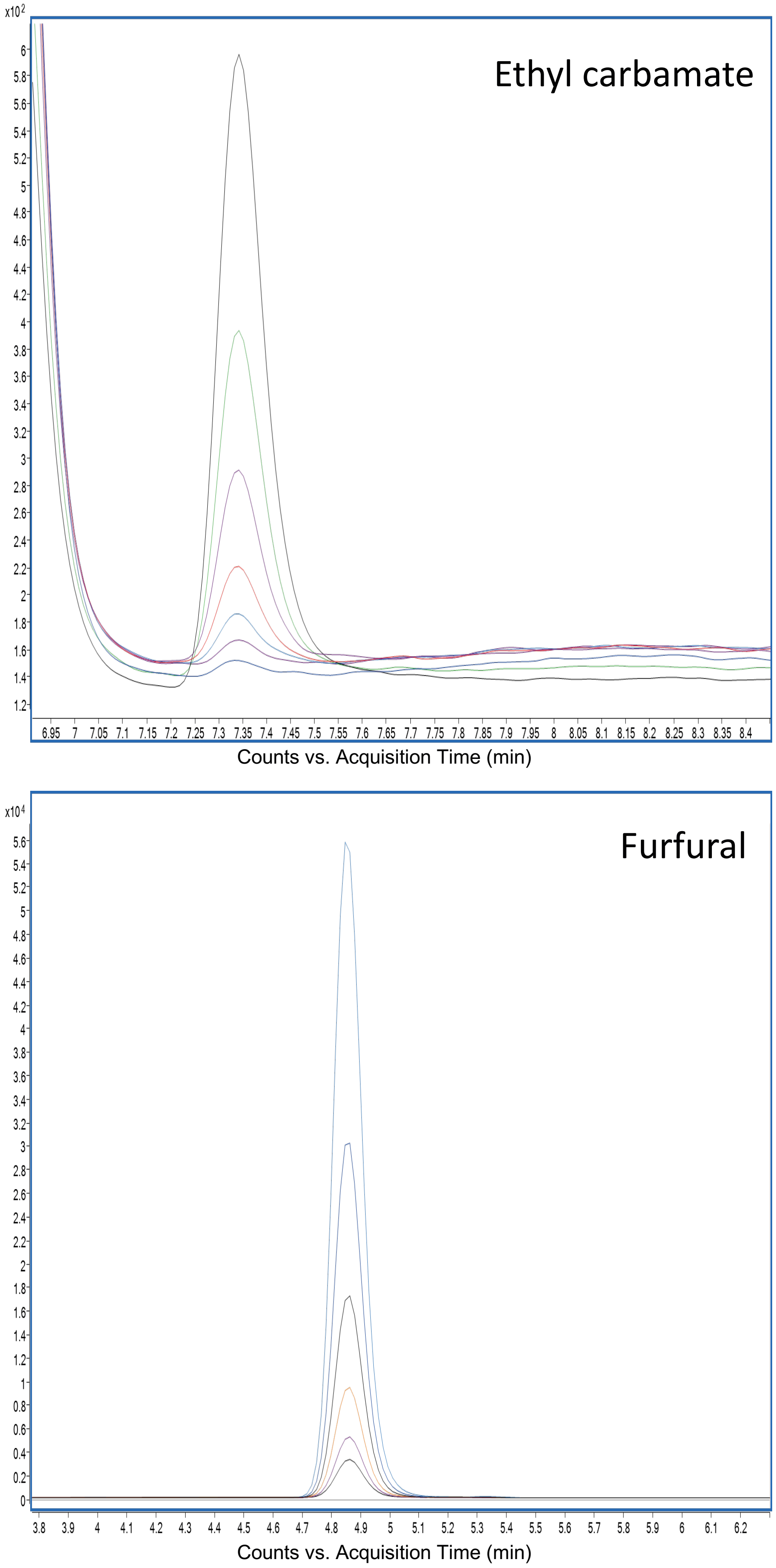

FIGURE 2. GC-MS chromatograms of ethyl carbamate and furfural.

TABLE 2. Detailed information for commercial Rakı samples.

Sample Code	Category	Suma Source	Alcohol Strength (% v/v)	Special mark on the label Application Notes
R1	Mass	Fresh grape/Raisin	45	-
R2	Mass	Fresh grape/Raisin	45	-
R3	Premium	100 % Fresh grape	50	-
R4	Low-end	Fresh grape/Raisin	43	-
R5	Mass	100 % Fresh grape	45	-
R6	Premium	100 % 100 % Raisin	47	Triple pot-still distillation
R7	Mass	100 % Fresh grape	43	-
R8	Premium	100 % Fresh grape	45	Triple pot-still distillation
R9	Mass	100 % Fresh grape	45	-
R10	Mass	100 % Fresh grape	45	Matured in oak barrels
R11	Premium	100 % Fresh grape	50	Single cycle
R12	Mass	100 % Fresh grape	45	Matured in oak barrels
R13	Mass	100 % Fresh grape	45	-
R14	Low-end	Fresh grape/Raisin	45	-
R15	Low-end	Fresh grape/Raisin	42	-
R16	Low-end	100 % fresh grape / Raisin	40	-
R17	Premium	100 % Fresh grape	47.5	Triple pot-still distillation
R18	Premium	Fresh grape/Raisin	45.5	-
R19	Premium	100 % Fresh grape	45	Single pot-still distillation
R20	Mass	Fresh grape	45	Matured in oak barrels
R21	Premium	100 % Fresh grape	45	Traditional
R22	Premium	100 % Fresh grape	45	-
R23	Premium	100 % Fresh grape	45	Matured in oak barrels
R24	Mass	Raisin	45	-
R25	Mass	Raisin	45	-
R26	Mass	Fresh grape/Raisin	45	-
R27	Mass	Fresh grape	45	-
R28	Premium	100 % Fresh grape	45	Triple pot-still distillation
R29	Premium	100 % Fresh grape	45	Triple pot-still distillation
R30	Premium	100 % Fresh grape	45	Triple pot-still distillation
R31	Low-end	Fresh grape/Raisin	43	-
R32	Mass	Fresh grape	45	-
R33	Mass	100 % Fresh grape	45	-
R34	Premium	Fresh grape	45	-
R35		Counterfeit Rakı	-	Alcohol + aroma
R36		Bogma (Illegal Rakı)	-	-
R37		Counterfeit Rakı	-	-

TABLE 3. Validation parameters for ethyl carbamate and furfural.

Compound	Calibration curve ($n = 7$)						
	Linearity range	Slope [(a)]	Intercept [(b)]	R^2 [(c)]	LOD [(d)]	ID [(e)]	Recovery (%)
Ethyl carbamate	5.5–350 µg/L	9.5	0	0.9995	0.38 µg/L	MS	98.3
Furfural	1–30 mg/L	13248	0	0.9962	0.02 mg/L	MS	99.2

[a b] Regression equation: y = ax + b, where y is the peak area and x is the concentration

[c] R^2, correlation coefficient.

[d] Limit of detection: calculated by signal-to-noise ratio.

[e] Identification. MS identified based on mass spectral library.

2.2. Alcohol strength and methanol analysis

2.2.1. Ethanol

The determination of ethanol volume in Rakı was carried out using a NIR spectrometer Anton Paar Alcolyzer (DMA 4500M-Alcolyzer ME). This NIR instrument comprises a LED light source, a multi-lens and a detector array. It has a temperature-controlled unit; the temperature of the samples were automatically adjusted to 20 °C. It can also be programmed to give the alcohol volume as a 2-digit percentage; the method was adapted from Darici and Cabaroglu (2018).

2.2.2. Methanol

An Agilent Technologies 7820A GC was used with a 5877B MSD (Santa Clara, CA, USA). A DB-WAX UI column (Agilent Technologies, Santa Clara, CA, USA) was used; it was 30 m long and 0.250 mm wide with an inner diameter of 0.25 µm. The initial oven temperature was set at 50 °C for 3 min, increased at a rate of 4 °C/min to 80 °C for 5 min, and then increased at a rate of 15 °C/min to a final temperature of 200 °C with 1 min of hold time. The injection volume for the analysis was 0.3 µL. The injection method was a split (20:1) method with an injection port temperature of 220 °C. The pressure of the injection port was set at 8.743 psi. The mass spectrometer source temperature was set at 240 °C and the quadrupole temperature set at 180 °C. The electron energy of the MS was set at 70 eV and the acquisition type was set to SIM and SCAN mode. For methanol, 31 m/z ions were measured and used for quantification. The method was adapted from Menevseoglu (2019).

2.3. Copper, arsenic, lead and zinc analysis by ICP-OES

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) analysis were conducted at Service Testing and Research Laboratory (STAR Lab) at the Ohio State University Wooster campus (Wooster, OH). Agilent 5110 ICP-OES Dual view model (Agilent Corp., Santa Clara, CA, USA) was used to determine metal contaminants in Rakı samples. The metals were quantified using the calibration models for each metal at a wavelength of 228 nm (As), 324 nm (Cu), 220 nm (Pb) and 206 nm (Zn), following a method modified from Budzynska *et al.* (2018).

RESULTS AND DISCUSSION

Table 4 shows the levels of ethyl carbamate (EC) in commercial Rakı. None of the Rakı samples contained EC. This may be due to the double distillation of Rakı, which can reduce EC levels by up to 80 % (Correa *et al.,* 2014). For instance, in whisky, only 1 % of EC can be formed during the second distillation (Riffkin *et al.,* 1989). Moreover, high concentrations of EC are generally found in stone-fruit alcoholic beverages produced from, for example, sour cherry and plum, because the process of breaking stones can initiate the formation of amygdalin-derived ethyl carbamate (Deak *et al.,* 2010). Brazilian distilled spirit Cachaça produced from sugar cane was reported to have a high level of EC: as much as 5589 µg/kg, which is above the permitted limit of 150 µg/kg (Andrade-Sobrinho *et al.,* 2002). A distilled spirit in China, Luzhou-flavour, had EC concentrations of between 17 and 151 µg/kg (Fang *et al.,* 2018).

Furfural (FR) levels in commercial Rakı are shown in Table 4. The range of FR levels was between undetectable and 3.97 mg/L, which is below the generally permitted limit (50 mg/L). Furfural contamination is found when the distillation continued after the tail part of the wine is reached. Therefore, carrying out the production steps carefully may help to reduce contamination. Commercial Rakı samples did not contain furfural, but three counterfeited Rakı samples had low amounts. In literature, many distilled spirits have been evaluated for their furfural concentrations;

TABLE 4. Ethyl carbamate, furfural, ethanol and methanol concentrations in commercial Rakı.

Samples	Ethyl carbamate (µg/kg)	Furfural (mg/L)	Ethanol (%)	Methanol (mg/100 ml)
R1	ND	ND	45.18 ± 0.12	34.17 ± 1.22
R2	ND	ND	45.16 ± 0.06	30.73 ± 0.56
R3	ND	ND	49.90 ± 0.24	24.69 ± 0.35
R4	ND	ND	42.88 ± 0.13	23.86 ± 0.11
R5	ND	ND	45.05 ± 0.22	38.12 ± 0.54
R6	ND	ND	47.15 ± 0.22	39.96 ± 0.35
R7	ND	ND	43.14 ± 0.15	37.54 ± 0.39
R8	ND	ND	45.07 ± 0.23	37.73 ± 0.44
R9	ND	ND	45.31 ± 0.25	39.31 ± 0.36
R10	ND	ND	44.96 ± 0.29	38.60 ± 0.87
R11	ND	ND	50.15 ± 0.14	25.52 ± 0.36
R12	ND	ND	45.03 ± 0.23	43.20 ± 0.14
R13	ND	ND	44.93 ± 0.21	23.87 ± 0.36
R14	ND	ND	45.11 ± 0.20	29.45 ± 0.55
R15	ND	ND	41.89 ± 0.33	31.90 ± 0.33
R16	ND	ND	40.18 ± 0.12	25.68 ± 0.21
R17	ND	ND	47.72 ± 0.30	42.82 ± 0.39
R18	ND	ND	45.54 ± 0.18	34.23 ± 0.11
R19	ND	ND	45.24 ± 0.20	40.49 ± 0.55
R20	ND	ND	45.10 ± 0.12	35.76 ± 0.29
R21	ND	ND	45.16 ± 0.16	52.63 ± 0.68
R22	ND	ND	44.95 ± 0.24	28.78 ± 0.23
R23	ND	ND	45.04 ± 0.08	45.38 ± 0.74
R24	ND	ND	45.22 ± 0.06	16.52 ± 0.19
R25	ND	ND	42.25 ± 0.08	16.35 ± 0.21
R26	ND	ND	45.02 ± 0.06	36.47 ± 0.54
R27	ND	ND	43.25 ± 0.19	14.55 ± 0.25
R28	ND	ND	47.14 ± 0.09	35.47 ± 0.39
R29	ND	ND	45.13 ± 0.24	12.36 ± 0.87
R30	ND	ND	45.10 ± 0.18	13.40 ± 0.65
R31	ND	ND	43.22 ± 0.21	43.85 ± 1.33
R32	ND	ND	43.06 ± 0.27	16.46 ± 0.78
R33	ND	ND	45.32 ± 0.11	46.22 ± 1.28
R34	ND	ND	45.12 ± 0.17	36.51 ± 0.56
R35	ND	3.97 ± 0.02	40.46 ± 0.11	ND
R36	ND	3.79 ± 0.02	56.91 ± 0.25	27.38 ± 0.36
R37	ND	2.06 ± 0.09	54.28 ± 0.32	48.85 ± 1.55

TABLE 5. Arsenic, copper, lead and zinc concentrations in commercial Rakı.

Samples	As (mg/L)	Cu (mg/L)	Pb (mg/L)	Zn (mg/L)
R1	<0.004	0.069	0.002	0.018
R2	<0.004	0.077	0.004	0.025
R3	<0.004	0.093	0.004	0.035
R4	<0.004	0.086	0.005	0.041
R5	<0.004	0.076	0.003	0.030
R6	<0.004	0.130	0.008	0.131
R7	<0.004	0.101	0.006	0.042
R8	<0.004	0.118	0.005	0.114
R9	<0.004	0.059	0.006	0.023
R10	<0.004	0.173	0.008	0.045
R11	<0.004	0.076	<0.002	0.020
R12	<0.004	0.161	0.008	0.024
R13	<0.004	0.101	0.004	0.033
R14	<0.004	0.074	0.003	0.022
R15	<0.004	0.066	0.004	0.024
R16	<0.004	0.073	0.003	0.045
R17	<0.004	0.079	0.006	0.046
R18	<0.004	0.138	0.003	0.032
R19	<0.004	0.199	0.003	0.032
R20	<0.004	0.130	0.006	0.041
R21	<0.004	0.414	0.005	0.058
R22	<0.004	0.253	0.026	0.392
R23	<0.004	0.310	0.007	0.157
R24	<0.004	0.060	0.003	0.020
R25	<0.004	0.153	0.010	0.076
R26	<0.004	0.242	0.005	0.029
R27	<0.004	0.050	0.003	0.019
R28	<0.004	0.071	0.003	0.011
R29	<0.004	0.077	0.004	0.026
R30	<0.004	0.046	<0.002	0.031
R31	<0.004	0.183	0.002	0.030
R32	<0.004	0.102	0.006	0.053
R33	<0.004	0.169	0.005	0.030
R34	0.0181	0.115	0.004	0.051
R35	0.0217	0.075	0.004	0.022
R36	<0.004	0.064	0.004	0.062
R37	<0.004	0.075	0.004	0.045

for example, sugarcane spirits from Brazil and Mozambique were found to contain 1.6–17 mg/L (Bortoletto and Alcarde, 2013) and 2.8–270 mg/L (Tabua *et al.,* 2018) respectively, and brandy and cognac were found to contain 0.5–82.5 mg/L (Tsakiris *et al.,* 2016) and 6.63 mg/L (Awad *et al.,* 2017) respectively. Our results show that commercial Rakı do not contain furfural, but adulterated ones have a low amount of furfural contamination. The ethanol levels of the Rakı samples are shown in Table 4. Commercial Rakı samples complied with regulations and the label. However, two Rakı samples, R36 and R37, which were not legally produced, had very high ethanol concentrations. Similarly, the methanol levels of the commercial Rakı complied with regulations. Only sample R35, a counterfeit Rakı, did not contain methanol since it was produced using an agricultural ethanol purified from some other alcohol.

Table 5 shows the metal contamination of Rakı samples. None of the samples contained arsenic, except for samples R34 and R35, which contained 0.018 mg/L and 0.022 mg/L respectively; these arsenic concentrations can be considered negligible. The absence of arsenic may be due to the arsenic-free copper alembics that was used during the production process. While arsenic is not common in distilled spirits, copper is problematic; it can, for example, catalyse the formation of ethyl carbamate, and the consumption of a high concentration of copper can produce toxic effects, such as diarrhea, excessive vomiting and liver damage (Silva *et al.,* 2020). In the present study, the concentrations of copper in the Rakı samples were low: between 0.046 and 0.414 mg/L, which is also below the limits for distilled spirits (i.e., 5 mg/L). Navarro (2007) reported copper concentrations in whisky, gin, rum, liquor, brandy, wine, and beer as being 1.01 mg/L, 0.1 mg/L, 2.34 mg/L, 0.59 mg/L, 8.01 mg/L, 0.39 mg/L and 0.39 mg/L respectively. Another toxic metal, Pb, was found at ppb levels in the commercial Rakı, most likely due to lead-free copper alembics. The permissible limit of Pb in alcoholic spirits in some European countries is in the range of 0.2–0.3 mg/L (Kostic *et al.,* 2010). Zinc concentrations of the Rakı was in the range of 0.01–0.39 mg/L. The permissible limit for zinc is 5 mg/L, thus Zn concentrations in the commercial Rakı were below the limit. The absence or a very low amount of zinc in the copper alembics could explain these results.

CONCLUSIONS

This study aimed to determine the chemical and metal contamination of commercial Rakı. Our results showed that neither ethyl carbamate nor furfural were detected in the commercial Rakı. The arsenic, copper, lead and zinc levels of the commercial Rakı were either below the limits or undetectable. In conclusion, the chemical and metal contamination of commercial Rakı is very low.

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