Determination of Cadmium and Chromium in Fruit Spirits Intended for Own Consumption Using Graphite Furnace Atomic Absorption Spectrometry

Mária Tatarková[1,*], Tibor Baška[1], Romana Ulbrichtová[1], Stanislav Kuka[1], Miroslava Sovičová[1], Eliška Štefanová[1], Eva Malobická[1], Henrieta Hudečková[1]

ABSTRACT

Introduction: Analysis of the occurrence of cadmium and chromium in selected samples of fruit spirits intended for own consumption.

Material and methods: In our pilot study, we analysed 89 samples of fruit spirits intended for own consumption. The samples were mineralized with use of microwave decomposition system MULTIWAVE 60 50 Hz and analysed by atomic absorption spectrometry with a graphite furnace (AAS GBC XPLORAA 5000 with GF 5000).

Results: Most of the analysed samples originated from plums (39), apples (38) and pears (5). The average ethanol concentration was 53.7%. Cadmium and chromium were detected in all samples. The highest concentration of chromium and cadmium was found in the apple spirit (31.9 ± 6.6 µg/l and 40.1 ± 8.3 µg/l).

Conclusions: The ethanol concentration in the samples was higher than in distribution spirits. Concentrations of chromium in all samples did not exceed the limit given by the Slovak legislation or the limit of the AMPHORA. The permissible cadmium concentration (10 µg/l according to the AMPHORA) was exceeded in 9 samples. This indicates the potential importance of cadmium compared to chromium. Due to the lack of information in this field, the study presents an important starting point for further research.

KEYWORDS

fruit spirits; cadmium; chromium; concentrations; analysis

AUTHOR AFFILIATIONS

[1] Department of Public Health, Jessenius Faculty of Medicine in Martin, Comenius University in Bratislava, Slovak Republic

[*] Department of Public Health, Jessenius Faculty of Medicine in Martin, Comenius University in Bratislava, Slovak Republic; e-mail: tatarkova12@uniba.sk

Received: 22 June 2021
Accepted: 6 December 2021
Published online: 4 March 2022

Acta Medica (Hradec Králové) 2021; 64(4): 213–217
https://doi.org/10.14712/18059694.2022.4

INTRODUCTION

The main risk factor in alcoholic beverages is ethanol, which has been classified as Group 1 (carcinogenic to humans) by the International Agency for Research on Cancer (IARC) in 2012. In terms of ethanol concentration, fruit spirits intended for own consumption present an increased risk because they usually have higher ethanol concentrations compared to alcoholic beverages in the distribution network (< 40% vol.) (1). In addition to the higher concentration of ethanol in fruit spirits intended for own consumption, presence of xenobiotics such as cadmium or chromium have been considered as another possible risk factors (2). There is an insufficient information about concentration of cadmium and chromium in alcoholic beverages intended for own consumption. The reason is that these alcoholic beverages fall only partially under regulatory control (determination of the volume of ethanol, methanol and higher alcohols) and are not subject to full regulatory control compared to alcoholic beverages in the distribution network.

The European project *"The European study Alcohol Measures for Public Health Research Alliance (AMPHORA)"* was dealing with the issue and pointed out relatively high mortality rate on alcohol attributable diseases in some countries (Hungary or Slovenia) only partially corresponding with amount of alcohol consumed (3). For this reason, several studies evaluated concentrations of certain possible contaminants. Among them, heavy metals can play a significant role at increased mortality rate on alcohol attributable diseases. IARC (International Agency for Research on Cancer) considers cadmium as a human carcinogen being associated with several types of cancer, e. g. liver, kidneys etc. Moreover, it is well known as a risk factor for cardiovascular diseases. Hexavalent chromium is associated with allergic reactions, skin irritation and lung and digestive tract cancer (4). At the same time, ethanol is also a significant risk factor for the above-mentioned diseases (2). There is possibility that the above diseases may occur due to the interaction of heavy metals with higher concentrations of ethanol, but current knowledge in this area is unknown.

The aim of this pilot study is to identify and measure the content of cadmium and chromium in various types of fruit spirits intended for own consumption originating from Slovakia. Another goal of the study was to evaluate the measured levels against the limits set by the AMPHORA project as well as valid Slovak legislation. The results significantly contribute to understand the extent of the issue and can present an important starting point for further systematic research in the field.

MATERIALS AND METHODS

SAMPLES

We analysed 89 samples of legal fruit spirits intended for own consumption. Samples were distilled in local growing distilleries in Martin (Northern Slovakia). The samples of fruit spirits were taken during the winter period 2018/2019. Most of the analysed samples were from plums (39), apples (38) pears (5) and apricots (2). We had only one sample from black elderberry, rose hip, cherry, grapes and raspberry.

The bottles were used to collect samples, which were soaked in 10% nitric acid for 24 hours with HNO_3 and afterwards washed twice with ultrapure water Type 1 (up H_2O) with minimum resistivity of 18.2 MΩ cm. The ethanol content was determined by alcoholometric tables. Samples were diluted (up H_2O) to 10% ethanol and mineralized by microwave decomposition system manufacturer (Multiwave 60 50 Hz) (Table 1). High-performance reaction vessels with pressure-activated-venting for routine and quality control applications made of PTFE-TFM with a volume of 40 ml were used for mineralization. Immediately before the mineralization, we prepared the 15 ml samples consisting of 10 ml trace metal grade (TMG) HNO_3 and 5 ml of 10% distillate. After mineralization, the mixture was made up to 15 ml with ultrapure H_2O. As stated by

Tab. 1 Digestion program of alcoholic beverages for MULTIWAVE 60 50 Hz.

Step	Ramp time (mm:ss)	Temp. (°C)	Hold time (mm:ss)	Fan
1	20:00	130	0:01	1
2	5:00	180	5:00	1
3		70		3

Tab. 2 Graphite furnace temperature program for the study of cadmium in spirits.

	Final Temp. (°C)	Ramp Time (s)	Hold Time (s)	Gas Type
1				
2	40	2.0	1.0	Inert
3	120	5.0	10.0	Inert
4	130	5.1	10.0	Inert
5	300	5.0	10.0	Inert
6	300	0.0	2.0	None
7	1800	1.0	1.5	None
8	2300	1.0	2.0	Inert

Tab. 3 Graphite furnace temperature program for the study of chromium in spirits.

	Final Temp. (°C)	Ramp Time (s)	Hold Time (s)	Gas Type
1				
2	40	5.0	10.0	Inert
3	90	10.0	10.0	Inert
4	120	10.0	10.0	Inert
5	1100	5.0	10.0	Inert
6	1100	0.0	2.0	None
7	2500	1.0	2.4	None
8	2900	1.0	2.0	Inert

the manufacturer, even at the 10% concentration limit, alcohols may strongly react with HNO_3 even in the cold. It is necessary let the mixture pre-react under the fume hood without closing and performing the digestion or use a safer method of sample preparation. Samples were analysed using a graphite furnace atomic absorption spectrometer (AAS GBC XplorAA 5000 with GF 5000) (Tables 2 and 3).

INSTRUMENTATION

Sample preparation consisted of previous mineralization (Multiwave 60 50 Hz). The samples were analysed by graphite furnace atomic absorption spectrometry using GBC XplorAA 5000 instrument equipped with GF 5000 graphite furnace. We used graphite cuvettes with a pyrolytic surface without a platform. We used the deuterium lamp background correction method. For specific cadmium analysis we used hollow cathode lamp with wavelength of 228.8 nm and lamp current 3 mA. For chromium we also used hollow cathode lamp, but with wavelength equal to 357.9 nm and lamp current 6 mA. The temperature program used to determine the cadmium by GF AAS is shown in Table 2. Chromium is in Table 3. The temperature mode has been set by the instrument manufacturer and adapted to measure the cadmium and chromium content in the presence of HNO_3. Argon was used as the inert gas at 300 ml/min.

CHEMICALS AND REAGENTS

In the analysis we used ultrapure water Type 1 (up H_2O) with minimum resistivity of 18.2 MΩ cm. Other used chemicals were nitric acid (trace metal grade – TMG HNO_3) and standard (Sigma-Aldrich: Cd; Sigma-Aldrich: Cr) for AAS with concentration of cadmium 1000 ± 4 µg/l and concentration of chromium 1000 ± 4 µg/l. The dosing volume of the sample without modifier was 25 µl and with modifier 20 µl. The modifier was used only for cadmium analysis. As the modifier, we used ammonium phosphate ($NH_4H_2PO_4$) in a volume of 5 µl according to the device manufacturer's recommendations. The standard for cadmium was diluted to 2.6 µg/l and for chromium was diluted to 16.0 µg/l (max. recommended concentration by AAS manufacturers). From each of these standard solutions, two additional calibration solutions with a quarter and a half concentration - three-point calibration - were programmed in the measuring device for each calibration. Blank was prepared from up H_2O. The concentration is expressed in µg/l. Limit of detection (LOD) and limit of quantification (LOQ) were different for each sample considering various dilution level (to achieve the same ethanol concentration before mineralisation).

RESULTS

Chromium was detected in all samples. The highest concentration of chromium was in the sample of the apple spirit K81 (31.9 ± 6.6 µg/l), K87 (31.6 ± 6.6 µg/l) and the pear spirit K31 (30.7 ± 6.4 µg/l). The average concentration of chromium in our samples was 19.1 ± 4.5 µg/l. Similarly, as chromium, cadmium was also detected in all samples. The highest concentration of cadmium was in the sample of the apple spirit K1 (40.1 ± 8.3 µg/l), the plum spirit K25 (30.8 ± 6.4 µg/l) and plum spirit K70 (23.8 ± 4.9 µg/l). The average concentration of cadmium in our samples was 6.0 ± 1.2 µg/l. The average concentration of ethanol was 53.7% (Table 4).

DISCUSSION

In the study, we compared our results with the standards set by Slovak legislation (5) as well as with the limits set by the AMPHORA project (3). According to the average ethanol concentration in all analysed samples (53.7%), we set the limit concentration of chromium at 462 µg/l, which was calculated from the limit value for chromium in other foods (0.5 mg kg^{-1}). This level was not exceeded. The AMPHORA project set the maximum concentration of chromium in alcoholic beverages at 500 µg/l, our results were not exceeded in any case. Following the application of the drinking water standard (50 µg/l), this concentration was not exceeded even in this case. All previous

Tab. 4 Results for Cr and Cd concentration in spirits.

Distilled fruit	Number of samples	Ethanol average (%)	Concentration of Cr (µg/l)			Concentration of Cd (µg/l)		
			Median	A. mean ± MU*	Range	Median	A. mean ± MU*	Range
plums	39	53.7	18.6	18.5	3.0–26.1	6.6	6.7 ± 1.4	<LOQ–30.8
apples	38	54.9	19.3	19.5 ± 4.1	12.9–31.9	4.8	5.8 ± 1.2	<LOQ–40.1
pears	5	51.4	19.5	21.8 ± 4.5	19.2–30.7	3.9	4.2 ± 0.9	2.1–6.7
apricots	2	46.0	19.3	19.4 ± 4.1	15.9–18.8	–	<LOQ	–
elder	1	43.2	14.7	14.8 ± 3.1	13.2–16.4	1.9	2.0 ± 0.4	1.9–2.3
grapes	1	52.6	19.6	19.6 ± 4.1	17.6–21.7	5.7	5.8 ± 1.2	5.2–6.5
cherries	1	49.8	22.3	22.3 ± 4.6	19.9–24.7	5.9	6.2 ± 1.3	5.5–7.2
raspberries	1	52.6	14.0	14.5 ± 3.0	13.0–16.6	1.5	2.1 ± 0.4	2.3–2.5
rose hip	1	52.4	18.5	19.0 ± 4.0	17.0–21.5	–	<LOQ	–

* arithmetic mean, ± measurement uncertainty (expanded uncertainty by 2), <LOQ lower than the limit of quantification

studies evaluating chromium concentrations in alcoholic beverages (wine, beer, spirits) consistently found out chromium present in very low concentrations in alcoholic beverages (2, 6). In a study by Lendinez et al. several types of alcoholic beverages were analysed, such as wine, beer, apple cider, brandy, rum whiskey, gin, vodka and aniseed liqueurs, with the highest concentration of chromium being 25.0 μg/l (6). In our results, the highest concentration of chromium was 31.9 ± 6.6 μg/l present in the sample of apple spirit, the average concentration of chromium was 19.1 ± 4.5 μg/l. Chromium concentrations in our samples did not exceed the limit value for drinking water. Considering our findings in the context of the findings of other studies and existing body of knowledge, chromium concentration in alcoholic beverages intended for own consumption is mostly not very high, generally not exceeding requirements for drinking water.

Similar as for chromium, according to the average ethanol concentration in all analysed samples (53.7%), we set the limit concentration of cadmium at 28 μg/l, which was calculated from the limit value for cadmium in alcoholic beverages (0.03 mg kg^{-1}) (5). This level was exceeded in two analysed samples, namely in the sample of apple spirit K1 (40.1 ± 8.3 μg/l) and in the sample of plum spirit K25 (30.8 ± 6.4 μg/l). The AMPHORA project determined the recommended limit in alcoholic beverages to be 10 μg/l (3). Concentrations lower than 10 μg/l were recorded in several cases taken, namely in 4 apple spirit samples: K65 (17.8 ± 3.7 μg/l), K52 (13.1 ± 2.7 μg/l), K50 (12.2 ± 2.5 μg/l) and K1 (40.1 ± 8.3 μg/l). In samples of plum spirits in 5 cases: K25 (30.8 ± 6.4 μg/l), K70 (23.8 ± 4.9 μg/l), K27 (18.3 ± 3.8 μg/l), K30 (15.4 ± 2.2 μg/l) and K49 (11.5 ± 2.4 μg/l).

Serbian study by Bonic et. al. evaluated cadmium in plum spirits. The cadmium concentrations in their study were below the limit of quantification (<LOQ). However, they defined, considering the used method, the limit of quantification more than 20 μg/l, which can be considered as a relatively high level (limit for cadmium concentration from AMPHORA project is set at 10 μg/l) (3, 7). Study Mena et al. evaluated cadmium in apple cider originating in Spain and the cadmium concentration varied between 0.2 μg/l and 0.7 μg/l (8). However, in our samples we found a considerably wider range with much more higher values extending from less than 0.6 μg/l up to 40.1 ± 8.3 μg/l. Two studies analysed samples of "orujo" distillate (a distillate made from grape marc) in Spain. Cadmium concentrations ranged from less than 0.01 to 1.9 μg/l (9) and from 1.0 to 1.9 μg/l (10). Again, compared to our grape samples (5.8 ± 1.2 μg/l), concentrations found in Spain were much lower. However, the main limitation of our result is small number of samples, as we only had one sample available.

From our results it is clear, that the concentrations of cadmium vary independently from ethanol concentration. As for as a role of used fruit, we can able to compare only plum and apple spirits due to a similar number of samples (39 samples of plum spirits and 38 of apple spirits). The mean cadmium concentration in plum spirits was 6.9 ± 1.4 μg/l and in apple spirits 6.1 ± 1.2 μg/l. The mean cadmium concentration from all samples was 6.0 ± 1.2 μg/l. The difference calculated from the average of cadmium in apple and plum spirits was 0.8 ± 0.2 μg/l, which is a higher value in plum spirits. This higher concentration of cadmium in plum spirits may be due to the presence of a fruit stone in the yeast (11). According to current knowledge, we know that the maximum concentration of cadmium in plum stones is 67 μg/kg, in peaches 6 μg/kg and in cherries 76 μg/kg (11). From the study by Y. Sultanbawa et al. it is known that the content of cadmium in the plum stones of *Terminalia ferdinandiana* was up to 100 μg/kg, from which we can assume the presence of cadmium in plum stones intended for yeast preparation in our samples (12). It is necessary to take into account that in our study we recorded only 8 cases of respondents who were pitting plums. A limitation in proving the effect of the fruit stone on the cadmium content in the final product is the lack of samples of plum spirits from fruit stone-free yeast and fruit stone-fermented yeast, so we cannot evaluate the effect responsibly. At the same time, in only two cases the respondents reported the growth of plums nearby public road, so we cannot evaluate the influence of this factor on the occurrence of cadmium concentrations either. The last significant factor of possible contamination of fruit spirits intended for own consumption is storage material intended for yeast. In neither case was a material other than plastic barrel used for the yeast, which means that the yeast was not exposed to the possibility of contamination from the surface treatment of the fermentation barrel.

CONCLUSIONS

Our study points out that the cadmium is a frequent contaminant of fruit spirits intended for own consumption, with concentrations above the recommended level of Slovak legislation and the limits of the AMPHORA project. Considering insufficient information on this issue, our results represent a significant insight as well as an important starting point for further research in this field.

FUNDING

This work was supported by grant UK/71/2017 from the University of Comenius in Bratislava.

REFERENCES

1. Lachenmeier DW. Is There a Need for Alcohol Policy to Mitigate Metal Contamination in Unrecorded Fruit Spirits?. Int J Environ Res Public Health 2020; 17(7): 2452.
2. WHO. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans VOLUME 96 Alcohol Consumption and Ethyl Carbamate. France: WHO, 2010: 1440.
3. AMPHORA. Alcohol Policy in Europe: Evidence from AMPHORA (relased 2012). (Accessed Jun 22, 2021, at http://www.drugs.ie/resourcesfiles/ResearchDocs/Europe/Research/2012/Alco_Policy_Euro_Evidence_From_Amphora_2012.pdf).
4. Vašková H, Kolomazník K. Spectroscopic measurement of trivalent and hexavalent chromium. 17th International Carpathian Control Conference (ICCC) 2016, 775–8.
5. MZ SR. Vyhláška č. 2/1994 Zb. ktorou sa ustanovujú hygienické požiadavky na cudzorodé látky v požívatinách.
6. Lendínez E. Determination of chromium in wine and other alcoholic beverages consumed in spain by electrothermal atomic absorption spectrometry. J AOAC Int 1998; 81(5): 1043–7.

7. Bonic M, Tesevic V, Nikicevic N, et al. The contents of heavy metals in Serbian old plum brandies. J Serbian Chem Soc 2013; 78(7): 933–45.
8. Mena C, Cabrera C, Lorenzo ML, et al. Cadmium levels in wine, beer and other alcoholic beverages: possible sources of contamination. Sci Total Environ 1996; 181(3): 201–8.
9. Solana RR, Salgado JM, Domínguez JM, et al. Assessment of minerals in aged grape marc distillates by FAAS/FAES. Food Control 2014; 35(1): 49–55.
10. Fariñas MV, García JB, Martín SG, et al. Direct determination of cadmium in Orujo spirit samples by electrothermal atomic absorption spectrometry: Comparative study of different chemical modifiers. Anal Chim Acta 2007; 591(2): 231–8.
11. Foulkes EC. Cadmium. Berlin: Springer-Verlag 1986: 400.
12. Sultanbawa Y, Chaliha M, Cusack A. et al. Monitoring the quality and bioactivity of Kakadu plum in the Northern Territory. Australia: AgriFutures Australia 2018: 170.