UNRECORDED ALCOHOL AS A POTENTIAL SOURCE OF CADMIUM EXPOSURE
NEZAZNAMENANÝ ALKOHOL AKO POTENCIÁLNY ZDROJ EXPOZÍCIE KADMIA

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ABSTRACT
Introduction: The lack of information about cadmium contamination of unrecorded plum spirits arouses the question of how this issue is relevant to public health.
Objective: The objective of the study is to detect cadmium in plum spirits and determine statistical significance factors, such as the place of cultivation distilled plums and volume of ethanol in final products.
Methods: We analysed 35 samples of legal unrecorded plum spirits. Samples were distilled in local growing distilleries in Martin (Northern Slovakia). Sample preparation consisted of previous mineralization using microwave decomposition system MULTIWAVE 60 50 Hz. The samples were analyzed by atomic absorption spectroscopy with graphic furnace (AAS GBC XPLORAA 5000 with GF 5000).
Results: Cadmium was detected in 34 samples. In 7 of them, the concentration was lower than the limit of quantitation (LOQ). The highest observed concentrations of cadmium were the sample from Ostruňa – the district of Kežmarok and Vrútky – the district of Martin (30.8 ± 9.04 µg/l and 23.77 ± 4.94 µg/l, respectively). The average ethanol concentration was 53.93 % and the average cadmium concentration was 7.04 ± 1.85 µg/l.
Conclusions: The results of our study point out to the cadmium as a contaminant of plum spirits with possible health effects. Given the account insufficient information on cadmium levels in unrecorded plum spirits, our results represent an important insight in the issue as well as an important starting point for further research.

Key words: Cadmium. Unrecorded alcohol. Plum spirits. Analysis

ABSTRAKT
Úvod: Nedostatok informácií o kontaminácií nezaznamenaných slivkových destilátov kadmiom vyvoláva otázku, do akej miery sa jedná o verejno-zdravotnícky problém.
Cieľ: Cieľom štúdie je zistiť prítomnosť kadmia v slivkových destilátoch a stanoviť štatisticky významné faktory, ako lokalita pestovania destilovaných sliviek a objem etanolu vo finálnych výrobkoch.
Metódy: Analyzovali sem 35 vzoriek legálnych nezaznamenaných slivkových destilátov. Vzorky boli destilované v lokálnych pestovateľských páleniciach v Martine (severné Slovensko). Príprava vzoriek pozostávala z predchádzajúcej mineralizácie prostredníctvom mikrovlnného rozkladného systému MULTIWAVE 60 50 Hz. Vzorky sa analyzovali atómovým absorpčným spektormetrom s grafitovou pieckou (AAS GBC XPLORAA 5000 s GF 5000).
Výsledky: Kadmium bolo zistené v 34 vzorkách. V 7 z nich bola koncentrácia nižšia ako limit kvantifikácie (LOQ). Najvyššie koncentrácia kadmia boli vo vzorke z Ostrune – okres Kežmarok a Vrútky – okres Martin (30,8 ± 9,04 µg/l a 23,77 ± 4,94 µg/l, v uvedenom poradí). Priemerná koncentrácia etanolu bola 53,93 % a priemerná koncentrácia kadmia bola 7,04 ± 1,85 µg/l.
Závery: Výsledky našej štúdie poukazujú na kadmium ako kontaminant slivkových destilátov s možnými účinkami na zdravie. Vzhľadom na nedostatočné informácie o hladinách kadmia v nezaznamenaných slivkových destilátoch naše výsledky predstavujú dôležitý náhľad do problematiky, ako aj dôležitý východiskový bod pre ďalší výskum.

Kľúčové slová: Kadmium. Nezaznamenaný alkohol. Slivkové destiláty. Analýza

INTRODUCTION

In general, the consumption of alcoholic beverages in Central and Eastern Europe is widespread. Although the majority of consumed beverages includes recorded alcohol, the consumption of unrecorded alcohol is significant as well [1]. The definition of unrecorded alcoholic beverages is currently inconsistent. Generally, unrecorded alcohol can be divided into legal or illegal. Among legal unrecorded alcohol we rank homemade fruit spirits, wine or beer. These alcoholic beverages are intended for own consumption (non-commercial alcohol) [2]. The regulatory measures for legal unrecorded alcohol are more rigorous in case of spirits (such as reporting production to the customs office, using approved distiller boilers, etc.) than regarding wine and beer (Act No. 290/2018 Coll.) [3]. Therefore, sprits intended for own consumption are only partially subject of governmental supervision (including namely quality of distillation apparatus, level of methanol, ethanol or higher alcohols) and a possible presence of other compounds, including carcinogenic ones such as cadmium is not standardly checked. Their effect can be further amplified by a relatively high concentrations of ethanol, compared against commercially distributed products [4-5]. Cadmium as well as ethanol are classified as “carcinogenic to humans” (group 1) by the International Agency for Research on Cancer (IARC). As for cadmium, there are legislative regulation regarding concentration of cadmium in food, drinking water and other commercial products intended for human consumption. However, there is insufficient information on cadmium levels in unrecorded alcoholic beverages and its potential public health impact.

The objective of the study is to detect the presence of cadmium in samples of plum spirits intended for own consumption distilled in local growing distilleries within environs of Martin (Northern Slovakia). This study provides a preliminary insight into the problem and provides information to estimate its potential relevance to public health.

MATERIALS AND METHODS

Samples

We analysed 35 samples of legal unrecorded alcoholic beverages with concentration of ethanol more than 40 %. Samples were distilled in local growing distilleries in the city of Martin (Northern Slovakia). The samples of distilled spirits were taken during the winter period 2018/2019. All samples of distilled spirits were distilled from plums.

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) (Tab. 1). 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 48 hours, the samples were analysed using a graphite furnace atomic absorption spectrometer (AAS GBC XplorAA 5000 with GF 5000) (Tab. 2).

Instrumentation

Sample preparation consisted of previous mineralization (Multiwave 60 50 Hz). The samples were analysed by atomic absorption spectrometer with graphic furnace type AAS GBC XplorAA 5000 with GF 5000.

For specific cadmium analysis we used hollow cathode lamp (228.8 nm wavelength, slit width of 0.5 nm, lamp current 3mA). The temperature program used to determine the cadmium by GF AAS is shown in Table 2 (the temperature mode has been set by the instrument manufacturer and adapted to measure the cadmium content in the presence of HNO_3).

Table 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

Table 2 Graphite furnace temperature program for the study of Cd in plum spirits

Steps of analysis	Final Temp.	Ramp Time	Hold Time	Gas Type
1	*	*	*	*
2	40	5.0	20.0	Inert
3	120	10.0	10.0	Inert
4	120	0.0	20.0	Inert
5	1300	5.0	10.0	Inert
6	1300	0.0	2.0	None
7	2500	1.0	2.4	None
8	2600	1.0	2.0	Inert

Legend: * sample injection

Argon was used as the inert gas at 300 ml/min (drying and ashing) except during the atomization step, the flow was stopped and 2.600 ml/min while cleaning condition

Chemicals and Reagents

In the analysis we used ultrapure water Type 1 (UP H_2O) with minimum resistivity of 18.2 MΩ.cm. Other chemicals were nitric acid (trance metal grade – TMG HNO_3) and standard (Sigma-Aldrich: Cd) for AAS with concentration of cadmium 1.000 ± 4 µg/l. As the modifier we used ammonium phosphate ($NH_4H_2PO_4$), as recommended by the instrument manufacturer. The standard for cadmium was diluted to 2.6 µg/l (max. recommended concentration by AAS manufacturers). Blank was prepared from UP H_2O. The cadmium 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). The limits were in the following intervals: LOD: 0.64 – 0.33 µg/l, LOQ: 0.99 – 1.91 µg/l.

RESULTS

Cadmium was detected in thirty-four samples of plum spirits (Tab. 3). In seven cases, the concentration was lower than the limit of quantitation (LOQ). The highest observed concentration of cadmium was found out in the sample of plum spirits from Ostruňa - district Kežmarok (30.8 ± 9.04 µg/l)

Table 3. Results for Cd concentration in plum spirits

Sample number	The origin of the plums	Place of plum cultivation	Ethanol (%)	Cd (µg/l)
1	Kežmarok	garden	52.0	30.80 ± 9.04
2	Martin	garden	70.7	23.77 ± 4.94
3	Žilina	garden	45.4	18.26 ± 0.53
4	Turčianske Teplice	garden	51.7	15.38 ± 3.20
5	Nové Zámky	garden	51.5	11.52 ± 2.40
6	Martin	garden	52.8	9.05 ± 1.86
7	Martin	garden	56.7	8.77 ± 1.60
8	Banská Štiavnica	garden	53.6	7.66 ± 1.60
9	Martin	garden	54.7	7.65 ± 1.59
10	Martin	garden	54.4	7.55 ± 1.57
11	Poľsko	-	66.9	7.54 ± 1.57
12	Žilina	garden	48.7	7.42 ± 1.55
13	Martin	garden	55.7	7.34 ± 1.53
14	Ružomberok	garden	53.8	7.31 ± 1.52
15	Martin	garden	50.0	7.31 ± 2.07
16	Martin	garden	53.0	7.19 ± 1.50
17	Žilina	garden	54.9	7.10 ± 1.48
18	Martin	garden	52.2	6.98 ± 1.45
19	Martin	garden	58.4	6.69 ± 1.39
20	Česká republika	-	53.0	6.67 ± 1.39
21	Martin	garden	52.2	6.37 ± 1.33
22	Partizánske	garden	50.4	6.37 ± 1.33
23	Myjava	garden	48.4	5.43 ± 1.13
24	Martin	garden	52.0	3.13 ± 0.89
25	Martin	garden	53.4	3.02 ± 0.63
26	Poľsko	-	59.9	2.32 ± 0.49
27	Kežmarok	garden	52.2	1.78 ± 0.50
28	Martin	garden	50.2	< 1.36*
29	Martin	garden	52.4	< 1.42*
30	Martin	garden	50.1	< 1.35*
31	Martin	garden	64.4	< 1.74*
32	Martin	garden	52.0	< 1.40*
33	Žilina	garden	55.7	< 1.50*
34	Martin	near the road	52.0	< 1.00*
35	Veľký Krtíš	garden	52.2	< 1.41*

* <LOQ- lower than the limit of quantification, ^{X} unknown place of plum cultivation

and in the sample from Vrútky – the district of Martin (23.77 ± 4.94 µg/l). The average ethanol concentration was 53.93 % and the average cadmium concentration was 7.04 ± 1.85 µg/l.

DISCUSSION

Nowadays, the production and consumption of fruit distillates spirits for own consumption such as plum and apple spirits have been evidenced increased attractively among people. It follows from effort of gardeners to process their own grown fruits and to have original products. Another motivation lies in effort to save money since such spirits come to cheaper than commercial products. This is also promoted by a recent change in legislation regar-ding conditions of licences for private distillate production (Act No. 290/2018 Coll.). Private distillate production is a subject of several legal conditions. The main ones are as follows: Only natural persons can produce private spirit; the distillate may be produced exclusively in a maximum volume of 100 l; only certified distillation apparatus should be used; fruit may be used exclusively from its own cultivation activity; spirits shall not be placed on the market or cannot by a subject of any commercial activity. The natural person must apply for inclusion into the register of private producers of spirits.

A natural person should to deliver to the customs office a notice of the production of the distillate three working days beforehand. The notice should include place, date and time of production of the spirits, type of fruit and quantity of ferment fruit as well as estimated total quantity of the spirits. The natural person must keep records of produced spirits etc. (Act No. 290/2018 Coll.) [3].

European data on cadmium content in spirits intended for own consumption are inconsistent and sparse because the most of available information is based only on pilot studies. Lachenmeier et. al., 2009 reported the highest cadmium concentration in spirits at 40.0 μg/l [6]. In the studies analysing spirits form Serbia [7] cadmium concentrations were below 20.0 μg/l. In the Romanian studies [8] cadmium was found in concentrations below 50 μg/l. In comparison with these results, we detected cadmium in overwhelming proportion of the samples with the maximum concentration as high as 30.8 μg/l. It indicates that cadmium is a frequent contaminant of fruit spirits. Differences in cadmium concentrations in fruit spirits can be caused by several factors such as fermentation quality, aging and storage of the final products, material of the distillation apparatus, etc. The quality of distilled fruits may be affected by the soil for growing, environmental pollution and use of pesticides or fertilizer in fruit growing. Final products may be contaminated from storage containers [9].

In our study, we did not show statistically significant differences in cadmium content in relation to growing sites, most probably due to the small size of samples coming from a road traffic area (only one sample with cadmium concentration < 1.00 μg/l). Similarly, the statistically significant correlation between cadmium concentration and ethanol level was not found. This fact may be due to a relatively high uniformity in ethanol concentration (most of the samples ranged 50-56 % of ethanol concentration).

CONCLUSIONS

Our study points out the cadmium as a contaminant of plum spirits with possible health effects. Considering the widespread consumption of plum spirits, which has a long tradition in Slovakia, the issue seems to be a potential public health problem. Taking into account insufficient information on this issue, our results represent a significant insight as well as an important starting point for further research in this field.

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