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Elemental composition and some optical characteristics of Bulgarian beers

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In this study, the concentrations of 14 elements in two brands of Bulgarian (three products of each) and a Romanian beer were determined. As a low alcoholic beverage, beer is often consumed in large quantities, therefore the concentration of the elements is compared with the rules for their content in drinking water. The fluorescence spectra for investigated samples are obtained at excitation wavelengths 250 nm, 300 nm, 350 nm, 400 nm, 450 nm and 500 nm. The zone of excitation at 450 nm gives emission between 500 nm - 600 nm. This zone is characteristic for vitamin B2 (riboflavin) emission and it can be attributed to flavins present in beer.

Keywords*: beer, essential elements, toxic elements, fluorescence spectra*

INTRODUCTION

The determination of heavy metals in beer is important for consumers. Relatively low concentrations of toxic elements affect human health. Elements such as Ni, Cd, As, Cr, Sb and Pb can lead to serious side effects. Although the content of Cd and Pb in drinks and food is usually low, we should not forget that can accumulate in biological systems, and have a long half-life. Arsenic occurs naturally in the environment or as a result of pollution caused by industrialisation. Most often, the environmental pollution with lead originates from anthropogenic activity. Content of lead, cadmium, mercury and arsenic in foods and beverages in most cases is regulated. The authors have never found mercury as a contaminant of food and drink home-produced in Bulgaria,

Beer is a complex mixture consisting mainly of water and ethanol with about 0.5% of dissolved solids [1]. Beer analysis is important for evaluation of its organoleptic characteristics, quality, nutritional aspects, and safety. The majority of methods require pre-treatment of samples and chemical reagents. The usefulness of optical methods is recognized, because their non-invasiveness, rapidity, sensitivity. They do not require chemical reagents.

The aim of this work is to determine the chemical composition and explore the possibilities of using fluorescence spectroscopy for further characterization of different brands of beer during storage.

EXPERIMENTAL

Samples:

Romanian beer (can)

Beer 1

- -unfiltered (glass bottle)
- -gold edge (glass bottle)
- -can (1)

Beer 2

- -unpasteurized (glass bottle)
- -special (glass bottle)
- -can (2)

Apparatus:

Inductively coupled plasma-mass spectrometer “X SERIES 2” – Thermo Scientific with 3 channel peristaltic pump; concentric nebulizer; Peltier-cooled spray chamber (4°C); Xt interface option; Ni cones and forward plasma power of 1400 W was used for the determination of Al, Mn, Fe, Zn, Cu, Co, Pb, Cd, As, Cr, Ni, Mo, Sb and Rb.

Content of the Fe, Cu, Mn and Zn in beers was further confirmed with a Prodigy 7 ICP-AES spectrometer (Teledyne Leeman).

Fluorescence measurements were made by the HORIBA Jobin Yvon Fluorolog-3 spectrofluorometer. The instrument is fully-computerized and uses a Xenon lamp as an excitation source. The wavelength range was set at 220-800 nm in excitation and emission. The slits were set at 3 nm and the increment was set at 1 nm for both excitation and emission measurements.

Reagents

Multi-element standard solution V for ICP (Fluka, Sigma-Aldrich) and 1000 mg L^{-1} As (Fluka, Sigma-Aldrich) were used for the preparation of diluted working standard solutions for calibration for ICP-MS measurements. Stock standard solutions of Fe, Cu, Mn and Zn (1.000 g L^{-1} (Merck)) were used for the preparation of diluted working standards for

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calibration for ICP-AES. Nitric acid (65%), (Suprapur, Merck) were used for sample digestions.

Method for digestion of samples

10 ml of sample was treated with 1 ml HNO_3 to remove the organic portion of the beer on a sand bath, and then again brought to 10 ml with distilled water. The same procedure is used to prepare a blank.

RESULTS AND DISCUSSION

The fluorescence spectra of two famous types of Bulgarian beers were investigated and were compared with the spectrum of Romanian beer. For this purpose the excitation-emission matrix were obtained in the region 290 nm - 750 nm.

The fluorescence spectra for investigated samples are obtained at excitation wavelengths 250 nm, 300 nm, 350 nm, 400 nm, 450 nm and 500nm. The ratio $I_{emission}/I_{exitation}$ is over 1 for short wavelength - 250 nm, 300 nm and 350 nm, for the other wavelengths the ratio is under 1.

The ratios for short wavelength 250 nm, 300 and 350 nm are very different, while for 400nm, 450 nm and 500nm $I_{emission}/I_{exitation}$ have close values. Hence, it can be concluded that short wavelengths are appropriate for investigation of different types of beer.

The fluorescence emission spectra for excitation wavelength 300 nm are presented on the figure 1.

The short-wavelength fluorescence, with excitation at 250 nm, 300 nm and 350 nm and emission between 420 nm and 520 nm, tentatively attributed to aromatic amino acids. The emission in region 420 nm - 450 nm may originate from components of the vitamin B group [2]. There is a difference in fluorescent spectra in the range 500-600 nm and excitation at 450 nm. That zone is characteristic for vitamin B2 (riboflavin) emission and can be attributed to flavins present in beer. This emission disappears in beer exposed to light, in accordance with the well-known photoinstability of flavins [3].

The fluorescence intensities at 520 nm were presented on the figure 2 at excitation wavelength 450 nm. The Bulgarian beers in cans demonstrated higher fluorescence intensity than the samples in glass bottles. Lower intensity of the Romanian beer most probably is determined by the lower content of determined components in raw materials.

Considering that beer contains about 90% water, the main source of microelements are barley, hops and yeast, as the water in use should follow regulations for drinking water. During the brewing process, the metal content of beer could be also affected by the components of the brewery equipment involved [4]. Beer is a low alcoholic beverage, usually consumed over 250 ml per drink, therefore the concentration of Cd, Cu, Cr, Ni, and As in the analyzed beers are tested against the permitted norms in water in Bulgarian regulations (Cu – 2000 µg L^{-1}, Fe - 200 µg L^{-1}, Mn – 50 µg L^{-1}, Cr – 50 µg L^{-1}, Ni – 20 µg L^{-1}, Pb - 10 µg L^{-1}, As – 10 µg L^{-1} and Cd - 5 µg L^{-1}). The permitted amount of Pb in low alcoholic beverages and wines is 0.20 mg kg^{-1}.

As seen in Table 1, there aren't major differences in Al concentration between glass bottles and cans, neither between the two brands of beer; as a reference concentration of Al in Spanish beers is around 36.5 - 795.2 µg L^{-1} [5]. Chromium concentration is below the recommendation for drinking water, and can be compared to what we can find in Italian beers [6]. Concentrations of Cu, Zn and Mn in the two brands are very similar, as copper concentration is close to the one found in the Spanish beers [7]. The only difference is Mn in unfiltered beer, which is 1.7 times higher than in other beers. The contents of Co, Mo, Fe, Sb and Rb do not differ in the two brands. Main differences with the Romanian beer are the concentrations of Cr, Cu, Mo and Rb.

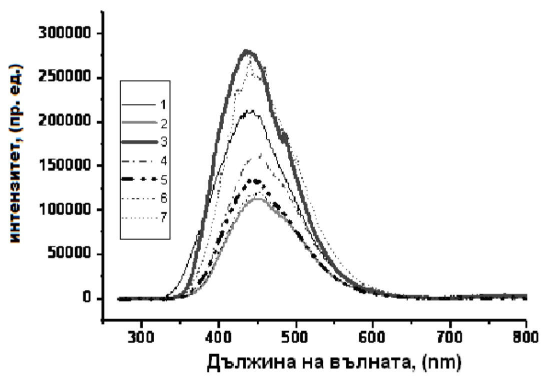

Fig. 1. Fluorescence spectra of beer samples for excitation wavelength 300 nm *1. Romanian beer - can, 2. gold edge, 3. unfiltered, 4. can (1), 5. unpasteurized, 6. special, 7. can (2)*

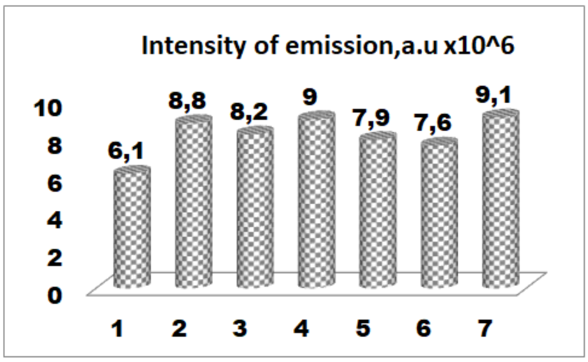

Fig. 2. Intensity of emission at 520 nm for beer samples at excitation at 450 nm.

Table 1. Concentration range of some elements in beer (RSD=1-7%)

Sample		Elements				
		Al, μg L^{-1}	Cr, μg L^{-1}	Cu, μg L^{-1}	Zn, μg L^{-1}	Mn, μg L^{-1}
Romanian		70-81	3-6	8-12	72-80	28-33
Beer 1	unfiltered	50-57	15-20	31-37	60-72	74-89
	gold edge	45-48	12-14	33-37	44-46	44-52
	(1)	45-49	10-13	46-52	83-103	47-53
Beer 2	unpasteurized	44-51	10-12	42-47	115-219	43-53
	special	52-66	8-12	50-58	48-68	44-57
	(2)	50-55	10-17	45-54	65-77	52-63
water - norm			***50***	***2000***		***50***

Table 1. (continue)

Sample		Elements				
		Co, μg L^{-1}	Mo, μg L^{-1}	Fe, μg L^{-1}	Sb, μg L^{-1}	Rb, μg L^{-1}
Romanian		0.1-0.2	10-13	112-127	0.3-0.5	61-69
Beer 1	unfiltered	0.2-0.3	4-5	81-92	0.3-0.6	104-112
	gold edge	0.2-0.4	3-4	104-153	0.4-0.6	112-120
	(1)	0.2-0.3	2-4	87-101	0.8-1.1	137-142
Beer 2	unpasteurized	0.1-0.2	1-3	83-112	0.6-1.0	112-128
	special	0.1-0.2	2-3	80-94	0.8-1.3	98-114
	(2)	0.1-0.3	3-4	86-90	1.2-1.4	125-150
water - norm				***200***		

Table 2. Concentration range of toxic elements in beer (RSD=3-7%)

Sample		Elements			
		As, μg L^{-1}	Cd, μg L^{-1}	Pb, μg L^{-1}	Ni, μg L^{-1}
Romanian		4-5	0.14-0.16	22-26	1-3
Beer 1	unfiltered	5-6	0.06-0.09	12-14	8-10
	gold edge	8-10	0.15-0.19	20-23	6-7
	(1)	5-7	0.05-0.06	17-20	8-9
Beer 2	unpasteurized	2-3	0.03-0.05	15-17	5-6
	special	2-4	0.06-0.08	13-15	5-6
	(2)	4-6	0.07-0.12	17-20	7-8
water - norm		***10***	***5***	***10***	***20***

Table 2 shows the concentrations of toxic elements in the beers. Only Pb concentrations are actually higher than the established norms for drinking water with beer having twice as much. The measured values of Pb in Bulgarian beers is close to or less than the reported values of Brazilian beers [8], but higher than different European ones [9]. As concentrations levels are close to what can be found in water, matching the reported values for Italian, Spanish and other beers [9, 10]. The Romanian beer is identical when it comes to the toxic elements, excluding Ni which has lower values.

CONCLUSIONS

Bulgarian beers are safe for consumption with concentrations of the determined elements mostly matching the norms for drinking water.

Can packages preserve beer's organic components better than glass bottle.

In the following investigations model can be obtained, which will correctly predict riboflavin and amino acids in beers. Fluorescence method may become a suitable alternative, giving accurate, rapid and less expensive results.

It would be interesting to identify correlations between fluorescent constituents and other components such as association of changes in Flavin with development of light struck flavor in beers upon exposure to light.

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