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The elemental profile of ciders made from different varieties of apples

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Abstract:
Macro- and microelements are vital components of the nutrient profile of apples and apple juice. Although the mineral composition of apple juices has been well studied, there is a lack of research into the elemental profile of ciders. We aimed to determine the concentrations of macro- and microelements in various samples of ciders.

We studied 25 experimental ciders from apple juice of direct extraction (fresh must) and 4 commercial ciders purchased from a retailer in Krasnodar. Mass concentrations of metal cations were determined by high-performance capillary electrophoresis, atomic absorption spectrometry with electrothermal atomization, and atomic emission spectrometry with inductively coupled plasma.

The concentrations of macroelements in the ciders from fresh must depending on the variety varied significantly in the following ranges (mg/L): 696–1920 for potassium; 6.7–26.8 for sodium; 4.3–35.5 for calcium; and 10.2–36.8 for magnesium. The commercial ciders had significantly lower concentrations of macroelements. The content of iron ranged from 0.86 to 2.26 mg/L. Among microelements, copper cations were detected in the range from 31.0 to 375 µg/L. The concentrations of toxic elements did not exceed the maximum permissible values in any of the samples, including the commercial ones. Finally, ranges of variation were established in the concentrations of macro- and microelements depending on the varietal characteristics of apples.

The pomological varieties of apples used in the study were grown under the same agrotechnical conditions. Therefore, the differences revealed in the elemental profile of the ciders were assumingly due to the genetic characteristics of the respective variety.

Keywords: Apple varieties, microelements, macroelements, concentration ranges, cider

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INTRODUCTION

According to numerous studies, the nutrient profile of apples and apple juice contains macroelements (potassium, calcium, magnesium, and sodium) and microelements (iron, zinc, copper, iodine, manganese, molybdenum, and fluorine). Their concentrations vary depending on the variety and location of the apple tree [1–4]. A number of studies also report the presence of so-called ultraelements in apples, including selenium, cobalt, and chromium [5, 6].

Fully or partially fermented apple juice is used to produce ciders – pleasantly refreshing beverages with a low alcohol content. Recent years have seen a growing consumer interest in cider in many European countries (France, Spain, Austria, Germany, Switzerland) and America. During alcoholic fermentation, the juice's profile undergoes significant changes in the concentrations of some elements, which is associated with the use of clay minerals for physical and chemical treatments [7–11]. Ciders are rich in various micro- and macro elements that come from apples, which, in their turn, obtain them directly from the soil. Therefore, their diversity largely depends on the mineral composition of the soil. Apple trees growing in calcic or siliceous soils contain calcium or silicon, which can sometimes be felt in the taste of cider.

Ciders also vary depending on the maturity of apples (more mature fruits are richer in microelements), the growing method (with or without mineral fertilizers), and processing technology. Although apple juices have been widely studied for their mineral composition, there has been insufficient research into the elemental composition of ciders [3, 12, 13]. Yet, it is important to know metal concentrations in cider not only to assess potential health risks for consumers, but also to evaluate the quality, origin, and authenticity of ciders [14–19].

Minerals have a high nutritional value in addition to their effect on the taste and various biochemical processes in ciders. For the human body, minerals are the most important components taking part in the main physiological processes in cells, organs, and tissues. Ciders contain so-called "essential elements" whose deficiency in the body disrupts its normal activity, development, and reproduction. They are iron, copper, zinc, cobalt, chromium, molybdenum, selenium, and manganese. Conditionally essential elements include actinium, boron, bromine, lithium, nickel, silicon, vanadium, and others.

We aimed to study the macro- and microelemental profile in ciders and to establish ranges of their mass concentrations.

STUDY OBJECTS AND METHODS

We studied apples of domestic and foreign selection, including those produced by the North-Caucasian Federal Scientific Center of Horticulture, Viticulture and Winemaking. The apples of various ripening stages were provided by the Tsentralnoye Experimental Farm (Krasnodar, Russia). The ploidy was 2n = 2x for most varieties and 2n = 3x for the Soyuz, Ekzotika, and Dzhin varieties. The apples typical in shape, color, and degree of maturity were collected from different sides of 3–5 trees for each variety according to the generally accepted method [14].

To produce ciders, the fruits were crushed in a homogenizer using the same processing mode. The must was fermented under laboratory conditions with the *Fruit* yeast race (genus *Saccharomyces cerevisiae*, Erbsle Geisenheim, Germany) at 18 ± 1°C. The ciders clarified spontaneously by settling, followed by sediment separation and filtration. The control samples were a semi-sweet carbonated pasteurized cider "Strongbow Rose" (Heineken United Breweries, St. Petersburg, Russia) prepared from fermented reconstituted apple juice; a carbonated sweet cider "Chester's" (Agroservis, Ramenskoye, Russia) from fresh apples grown in the Lipetsk region; as well as a semi-sweet "Greenvill Natural" (Kazakhstan) and "Cidre Royal" (Belarus) both produced from directly extracted juice.

Mass concentrations of potassium (K), calcium (Ca), sodium (Na), and magnesium (Mg) were determined by high-performance capillary electrophoresis according to the method developed by Scientific Center of Winemaking and the Instrumental and Analytical Center for Collective Use at the North-Caucasian Federal Scientific Center of Horticulture, Viticulture and Winemaking (certificates No. 61-10 dated 01.01.2010 and No. 60-10 dated 10.20.2010) using a Kapel-105M apparatus (Lumeks, Russia). This method is based on the separation of ions due to their different electrophoretic mobility during migration through a quartz capillary in an electrolyte under the influence of an electric field, followed by detection in the ultraviolet region at 254 nm.

Mass concentrations of copper (Cu), zinc (Zn), manganese (Mn), molybdenum (Mo), rubidium (Rb), and cesium (Cs) were determined by atomic absorption spectrometry with electrothermal atomization on a Kvant-Z.ETA spectrometer (KORTEK, Russia) according to State Standard R 51309-99. The method measures the absorption of resonance wavelength radiation by the atomic vapor of an element resulting from the electrothermal atomization of the sample under analysis in the graphite furnace of the spectrometer.

Mass concentrations of nickel (Ni), titanium (Ti), tin (Pn), cadmium (Cd), lead (Pb), arsenic (As), and mercury (Hg) were determined by inductively coupled plasma atomic emission spectrometry using an iCAP 7400 spectrometer (Thermo Scientific, USA) according to State Standard 30178-96. This method measures the intensity of the atomic radiation of the elements being determined, when the sample under analysis is sprayed into argon plasma inductively excited by a radio-frequency electromagnetic field. The samples were prepared by acid (nitric and hydrochloric) mineralization at elevated pressure according to State Standard R 53150–2008. For calibration, state standard reference samples of aqueous solutions were used with certified nominal values of mass concentrations and a relative error under ± 1% at $P = 0.95$. The sensory characteristics of the samples were evaluated on a 100-point scale by a panel at the Vinodelie (Winemaking) Scientific Center at the North-Caucasian Federal Scientific Center of Horticulture, Viticulture and Winemaking. Microsoft Excel 2019 and Statistika V.10.1 were used for statistical data processing by the analysis of variance.

RESULTS AND DISCUSSION

Table 1 presents experimental data on the concentrations of macroelements in ciders, which usually include cations of alkaline elements and alkaline earth elements.

We found significant differences in the concentrations of all macronutrients, including iron, depending on the variety of apples used to make the cider. The maximum and minimum concentrations of each cation differed several times: 2.6 times for potassium, magnesium, and iron, 6.6 times for sodium, and 8.3 times for calcium. Since the apples were grown in similar soils and using similar cultivation methods, such differences can only be due to their genetic characteristics and the ability of the trees to interact with the soil components.

Potassium was over 1 g/dm^3 in the ciders from the following varieties of apples (in descending order): Virginia (crab apple), Orfey, Ketni (crab apple), Persikovoye, Dzhin, Bagryanets Kubani, Margo, Florina, Zolotoye Letneye, and Enterprise. Its lowest concentration

Table 1 Mass concentrations of macroelements in ciders

No.	Name of sample	Mass concentration of alkaline and alkaline earth metal cations, mg/L			
		K	Na	Mg	Ca
		Varietal ciders from different pomological varieties of apples			
1	Ekzotika	895 ± 90	21.7 ± 2.4	23.6 ± 2.6	17.8 ± 1.8
2	Dzhin	1350 ± 135	31.3 ± 3.4	36.8 ± 4.0	35.5 ± 3.6
3	Enterprise	1090 ± 109	25.6 ± 2.8	17.8 ± 2.0	10.7 ± 1.1
4	Liberti	969 ± 97	16.1 ± 1.8	15.0 ± 1.7	7.2 ± 0.7
5	Karmen	760 ± 76	13.6 ± 1.5	19.1 ± 2.1	13.8 ± 1.4
6	Renet Platona	792 ± 79	6.7 ± 0.7	25.2 ± 2.8	9.9 ± 1.0
7	Bagryanets Kubani	1120 ± 112	18.0 ± 2.0	18.0 ± 2.0	13.3 ± 1.3
8	Soyuz	874 ± 87	8.3 ± 0.9	27.4 ± 3.0	11.8 ± 1.2
9	Ligol	704 ± 70	9.7 ± 1.1	17.5 ± 1.9	19.9 ± 2.0
10	Lyubimoye Dutovoy	696 ± 70	19.7 ± 2.2	20.6 ± 2.3	26.7 ± 2.7
11	Azimut	915 ± 92	21.3 ± 2.3	18.1 ± 2.0	16.8 ± 1.7
12	Margo	1120 ± 112	10.3 ± 1.1	15.8 ± 1.7	11.3 ± 1.1
13	Persikovoye	1370 ± 137	38.8 ± 4.3	17.7 ± 1.9	10.4 ± 1.0
14	Virginia	1920 ± 192	44.1 ± 4.9	33.7 ± 3.7	27.7 ± 2.8
15	Amulet	989 ± 99	34.3 ± 3.8	18.3 ± 2.0	9.8 ± 1.0
16	Orfey	1830 ± 183	42.3 ± 4.7	28.2 ± 3.1	13.9 ± 1.4
17	Ketni	1380 ± 138	41.0 ± 4.5	25.8 ± 2.8	34.0 ± 3.4
18	Champion	747 ± 75	26.5 ± 2.9	16.3 ± 1.8	15.5 ± 1.6
19	Zolotoye Letneye	1010 ± 101	36.6 ± 4.0	20.5 ± 2.3	10.1 ± 1.0
20	Prikubanskoye	847 ± 85	20.7 ± 2.3	14.7 ± 1.6	14.4 ± 1.4
21	Florina	1120 ± 112	25.4 ± 2.8	22.7 ± 2.5	16.7 ± 1.7
min		696 ± 70	6.7 ± 0.7	14.7 ± 1.6	9.8 ± 1.0
max		1920 ± 192	44.1 ± 4.9	36.8 ± 4.0	35.5 ± 3.6
		Varietal ciders from various apple tree forms			
22	12/1-20-16	1270 ± 127	26.8 ± 2.9	15.4 ± 1.7	5.5 ± 0.6
23	12/2-21-15	1060 ± 106	9.1 ± 1.0	26.4 ± 2.9	42.3 ± 4.2
24	12/2-21-36	900 ± 90	22.7 ± 2.5	10.2 ± 1.1	4.3 ± 0.4
25	12/3-2-6	853 ± 85	21.1 ± 2.3	10.7 ± 1.2	6.3 ± 0.6
min		696 ±70	9.1 ± 1.0	10.2 ± 1.1	4.3 ± 0.4
max		1270 ± 127	26.8 ± 2.9	26.4 ± 2.9	26.7 ± 2.7
		Commercial ciders			
26	Strongbow Rose	375 ± 38	138 ± 15	26.1 ± 2.9	24.2 ± 2.4
27	Chester's	520 ± 52	114 ± 13	36.3 ± 4.0	62.0 ± 6.0
28	Greenvill Natural	580 ± 58	92 ± 10	46.3 ± 5.1	55.0 ± 6.0
29	Cidre Royal	610 ± 61	68 ± 7	43.1 ± 4.7	64.0 ± 6.0
min		375 ± 38	68 ± 7	26.1 ± 2.9	24.2 ± 2.4
max		610 ± 61	138 ± 15	46.0 ± 5.1	64.0 ± 6.0

(700–800 mg/L) was found in the ciders from Ligol, Lyubimoye Dutovoy, Champion, Karmen, and Renet Platona. In the commercial ciders, potassium varied in the range from 375 to 610 mg/L. This difference can be explained by the production technology: a greater content of potassium was in the ciders made from directly extracted juice.

Sodium concentrations, on the contrary, were higher in the ciders from juice concentrates reconstituted with softened water. It might be that sodium-cation exchange resins were used in the sample under analysis to regulate the hardness, resulting in calcium and magnesium ions being replaced with sodium ions. The highest sodium content (> 40 mg/L) was found in the ciders from Virginia, Orfey, and Ketni varieties, while the lowest content (< 10 mg/L) was found in the samples from Renet Platona, Soyuz, Ligol, and from the 12/2-21-15 apple tree.

Calcium and magnesium cations play an important role in plant development, particularly in the functioning of the root system [18]. Calcium enhances plant metabolism, affects the conversion of nitrogenous substances, and accelerates the breakdown of storage proteins. In addition, it is essential for cell membranes and a good acid-base balance in plants. Magnesium, the central molecule of chlorophyll, is involved in photosynthesis and is part of pectin and phytin. Magnetosynsium deficiency decreases the content of chlorophyll in the green parts of the plant.

Many researchers believe that calcium and magnesium concentrations depend on the ability of the plant to absorb these elements from the soil. With other conditions being equal (e.g., the place of growth, cultivation method, or fertilizers), calcium and magnesium concentrations in the fruits and processing products may differ depending on the genetic characteristics of the variety, the development of its root system, and the plant's metabolism. According to our experimental data (Table 1), the largest amount of magnesium cations (> 25 mg/L) was in the ciders from Dzhin, Virginia, Orfey, Ketni, Renet Platona, and Soyuz varieties. The highest content of calcium (> 5 mg/L) was found in the ciders from Dzhin, Ketni, and Virginia.

Iron is involved in such vital processes as DNA synthesis, respiration, and photosynthesis [19]. It participates in various biochemical reactions catalyzed by enzymes, being their non-protein part (catalase, peroxidase). Due to its redox properties, iron is involved in the transfer of electrons and enzymes. According to Fig. 1, the maximum concentrations of iron (> 2 mg/L) were found in the samples from the following varieties: Virginia, Ketni, Soyuz, Liberti, and the 12/1-20-16 apple tree. This might be the reason why the juices from these varieties quickly changed their color from light golden to light brown during processing.

The commercial ciders had significantly lower concentrations of iron than the experimental samples prepared without technological treatments. This difference can be explained by the fact that in manufacturing facilities cider blends are demetallized to prevent ferric tannate haze.

The contents of microelements in the ciders from different apple varieties are shown in Table 2. Considering that neither juices nor ciders were subjected to any treatment in addition to alcoholic fermentation, which underwent under the same conditions, we can assume that the identified trends are also characteristic of apple fruits. Most microelements ensure normal growth and development of plants. They are involved in such vital processes as photosynthesis (manganese, iron, copper), respiration (manganese, iron, copper, zinc, copper), as well as carbohydrate, fat, and protein metabolism and the formation of organic acids and enzymes (manganese, copper, nickel, molybdenum, zinc). Microelements also bind free nitrogen (molybdenum, manganese, iron), convert nitrogen and phosphorus compounds (zinc, copper, manganese, molybdenum), participate in the development of nodule bacteria (copper, molybdenum), and catalyze various biochemical reactions (iron, manganese, molybdenum, copper, zinc, etc.) [20, 21]. Copper, cobalt, molybdenum, and zinc protect frost-resistant and drought-resistant plant species and contribute to a high level of protein synthesis. Zinc and manganese provide plant resistance to sudden temperature fluctuations. Molybdenum slows down water movement in plants during the day and accelerates it in the morning. It also increases the content of bound water and reduces the daytime depression of photosynthesis. Zinc and copper make plants more frost-resistant.

Microelements are mainly accumulated in the roots and their concentrations in fruits may indicate the intensity of metabolic processes in the root system. We found significant differences in the concentrations of microelements. In particular, the minimum and maximum concentrations differed 5.4 times for copper, 1.8 times for zinc, 4.6 times for manganese, 18 times for molybdenum, 1.9 times for rubidium (Fig. 2), 11.2 times for cesium, 14.8 times for nickel, 5.4 times for titanium, 5.9 times for lead, and 2.4 times for cadmium.

In the commercial samples, especially those made from directly extracted juice, the concentration of copper varied in about the same range as in the experimental samples, with much lower concentrations of other microelements. The ciders made from concentrated apple juice did not contain any manganese, molybdenum, or nickel, and the concentration of rubidium in them was 5–8 times lower compared to the ciders from directly extracted juice. Thus, the concentrations of microelement cations can be indicative of a relationship betweenthe cider and the composition of the soil on which the apple trees were grown. They can also be used as a marker of the beverage's origin.

According to our comparative analysis, the highest concentration of copper (> 200 μg/L) was found in the samples from Ekzotika, Dzhin, Amulet, and Prikubanskoye varieties, as well as from the 12/2-21-36 apple tree. The highest content of zinc (180–213 μg/L) was recorded in the ciders from Soyuz, Liberti, Ekzotika, and Bagryanets Kubani, as well as from the 12/2-21-36 tree. Manganese was abundant (> 90 μg/L) in the samples

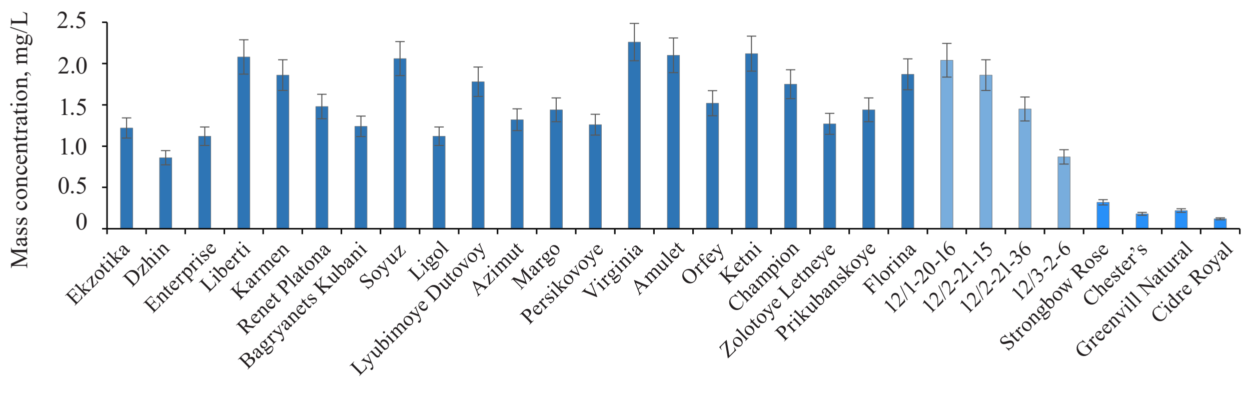

Figure 1 Mass concentrations of iron cations in ciders

Table 2 Mass concentrations of microelements in ciders

No.	Name of sample	Mass concentration of microelements, µg/dL								
		Cu	Zn	Mn	Mo	Cs	Ni	Ti	Pb	Cd
		Varietal ciders from different pomological varieties of apples								
1	Ekzotika	376 ± 56	190 ± 25	197 ± 35	11.3 ± 1.7	1.7 ± 0.3	10.9 ± 1.6	1.9 ± 0.3	8.4 ± 1.5	8.4 ± 1.3
2	Dzhin	222 ± 33	113 ± 15	213 ± 38	53.1 ± 8.0	0.2 ± 0.1	12.5 ± 1.9	0.5 ± 0.1	14.6 ± 2.6	6.2 ± 0.9
3	Enterprise	188 ± 28	162 ± 21	87 ± 16	34.1 ± 5.1	0.5 ± 0.1	32.4 ± 4.9	1.1 ± 0.2	17.6 ± 3.2	7.6 ± 1.1
4	Liberti	158 ± 24	196 ± 26	113 ± 20	27.5 ± 4.1	0.4 ± 0.1	27.4 ± 4.1	0.5 ± 0.1	21.3 ± 3.8	10.2 ± 1.5
5	Karmen	125 ± 19	157 ± 20	68 ± 12	20.5 ± 3.1	1.5 ± 0.3	16.6 ± 2.5	0.5 ± 0.1	18.7 ± 3.4	7.3 ± 1.1
6	Renet Platona	117 ± 18	175 ± 23	90 ± 16	17.9 ± 2.7	2.5 ± 0.5	2.4 ± 0.4	1.4 ± 0.2	12.7 ± 2.3	5.2 ± 0.8
7	Bagryanets Kubani	71 ± 11	195 ± 25	57 ± 10	14.5 ± 2.2	1.4 ± 0.2	6.8 ± 1.0	1.5 ± 0.2	16.5 ± 3.0	6.6 ± 1.0
8	Soyuz	100 ± 15	200 ± 26	70 ± 13	13.4 ± 2.0	1.6 ± 0.3	27.1 ± 4.1	1.9 ± 0.3	22.6 ± 4.1	8.6 ± 1.3
9	Ligol	129 ± 19	128 ± 17	112 ± 20	12.5 ± 1.9	1.2 ± 0.2	8.3 ± 1.3	1.5 ± 0.2	16.1 ± 2.9	11.2 ± 1.7
10	Lyubimoye Dutovoy	51 ± 8	88 ± 12	212 ± 38	9.0 ± 1.4	1.9 ± 0.3	12.8 ± 1.9	1.4 ± 0.2	5.6 ± 1.0	4.8 ± 0.7
11	Azimut	121 ± 18	165 ± 21	154 ± 28	7.2 ± 1.1	1.6 ± 0.3	18.4 ± 2.8	1.7 ± 0.3	3.8 ± 0.7	7.6 ± 1.1
12	Margo	175 ± 26	149 ± 19	56 ± 10	12.2 ± 1.8	2.2 ± 0.4	15.2 ± 2.3	2.1 ± 0.3	14.2 ± 2.6	7.3 ± 1.1
13	Persikovoye	97 ± 15	152 ± 20	55 ± 10	10.9 ± 1.6	0.8 ± 0.2	11.1 ± 1.7	2.4 ± 0.4	11.8 ± 2.1	5.9 ± 0.9
14	Virginia	108 ± 16	157 ± 20	117 ± 21	8.9 ± 1.3	1.6 ± 0.3	34.2 ± 5.1	2.3 ± 0.4	19.4 ± 3.5	11.7 ± 1.8
15	Amulet	201 ± 30	170 ± 22	174 ± 31	30.8 ± 4.6	2.8 ± 0.5	21.4 ± 3.2	2.0 ± 0.3	14.2 ± 2.6	9.5 ± 1.4
16	Orfey	82 ± 12	168 ± 22	63 ± 11	20.6 ± 3.1	2.9 ± 0.5	36.8 ± 5.5	2.4 ± 0.4	11.8 ± 2.1	8.3 ± 1.2
17	Ketni	71 ± 11	114 ± 15	141 ± 25	15.2 ± 2.3	1.1 ± 0.2	26.5 ± 4.0	2.5 ± 0.4	18.3 ± 3.3	9.6 ± 1.4
18	Champion	74 ± 11	193 ± 25	146 ± 26	13.2 ± 2.0	1.4 ± 0.3	31.4 ± 4.7	1.3 ± 0.2	17.8 ± 3.2	10.7 ± 1.6
19	Zolotoye Letneye	90 ± 14	175 ± 23	165 ± 30	12.0 ± 1.8	2.6 ± 0.5	19.2 ± 2.9	0.6 ± 0.1	14.6 ± 2.6	5.5 ± 0.8
20	Prikubanskoye	201 ± 30	170 ± 22	174 ± 31	30.8 ± 4.6	2.7 ± 0.5	16.5 ± 2.5	2.8 ± 0.4	9.2 ± 1.7	6.4 ± 1.0
21	Florina	82 ± 12	168 ± 22	63 ± 11	20.6 ± 3.1	2.9 ± 0.5	28.5 ± 4.3	1.5 ± 0.2	14.6 ± 2.6	8.9 ± 1.3
min		71 ± 11	88 ± 15	55 ± 10	7.2 ± 1.1	0.3 ± 0.1	2.4 ± 0.4	0.5 ± 0.1	3.8 ± 0.7	4.8 ± 0.7
max		376 ± 56	200 ± 30	213 ± 38	53.0 ± 8.0	2.9 ± 0.5	36.8 ± 5.5	2.8 ± 0.4	22.6 ± 4.1	11.7 ± 1.8
		Varietal ciders from various apple tree forms								
22	12/1-20-16	36.7 ± 5.5	159 ± 21	46.1 ± 8.3	6.3 ± 0.9	1.5 ± 0.3	23.1 ± 3.5	1.1 ± 0.2	4.6 ± 0.8	6.4 ± 1.0
23	12/2-21-15	109 ± 16	156 ± 20	192 ± 35	9.8 ± 1.5	2.2 ± 0.4	8.7 ± 1.3	2.2 ± 0.3	3.8 ± 0.7	8.0 ± 1.2
24	12/2-21-36	35.6 ± 5.3	214 ± 28	75 ± 14	8.0 ± 1.2	1.8 ± 0.3	14.1 ± 2.1	1.9 ± 0.3	4.4 ± 0.8	7.3 ± 1.1
25	12/3-21-6	31.1 ± 4.7	138 ± 18	71.1 ± 13.0	6.8 ± 1.0	1.1 ± 0.2	21.3 ± 3.5	0.9 ± 0.1	4.5 ± 0.8	5.2 ± 0.8
min		31.1 ± 4.7	138 ± 18	46.1 ± 8.3	6.3 ± 0.9	1.1 ± 0.2	8.7 ± 1.3	0.9 ± 0.1	3.8 ± 0.7	5.2 ± 0.8
max		109 ± 16	214 ± 28	192 ± 35	9.8 ± 1.5	2.2 ± 0.4	23.3 ± 3.5	2.2 ± 0.3	4.6 ± 0.8	8.0 ± 1.2
		Commercial ciders								
26	Strongbow Rose	210 ± 32	10.2 ± 1.3	< 1.0*	< 1.0*	0.2 ± 0.1	< 1.0*	0.2 ± 0.1	1.2 ± 0.2	2.1 ± 0.3
27	Chester's	252 ± 38	45.3 ± 5.9	86 ± 16	14.3 ± 2.0	0.3 ± 0.1	4.6 ± 0.7	0.5 ± 0.1	1.8 ± 0.3	4.6 ± 0.7
28	Greenvill Natural	371 ± 56	54 ± 7	73 ± 13	18.4 ± 2.8	0.3 ± 0.1	11.3 ± 1.7	0.4 ± 0.1	2.4 ± 0.4	5.8 ± 0.9
29	Cidre Royal	311 ± 47	60 ± 8	113 ± 20	16.4 ± 2.5	0.5 ± 0.1	13.6 ± 2.0	0.3 ± 0.1	3.6 ± 0.6	6.2 ± 0.9
min		210 ± 32	10.2 ± 1.3	< 1.0*	< 1.0*	0.2 ± 0.1	< 1.0*	0.2 ± 0.1	1.2 ± 0.2	2.1 ± 0.3
max		371 ± 56	60 ± 8	113 ± 20	18.4 ± 2.8	0.5 ± 0.1	13.6 ± 2.0	0.5 ± 0.1	3.6 ± 0.6	6.2 ± 0.9

*The value is below the lower limit of the detection range

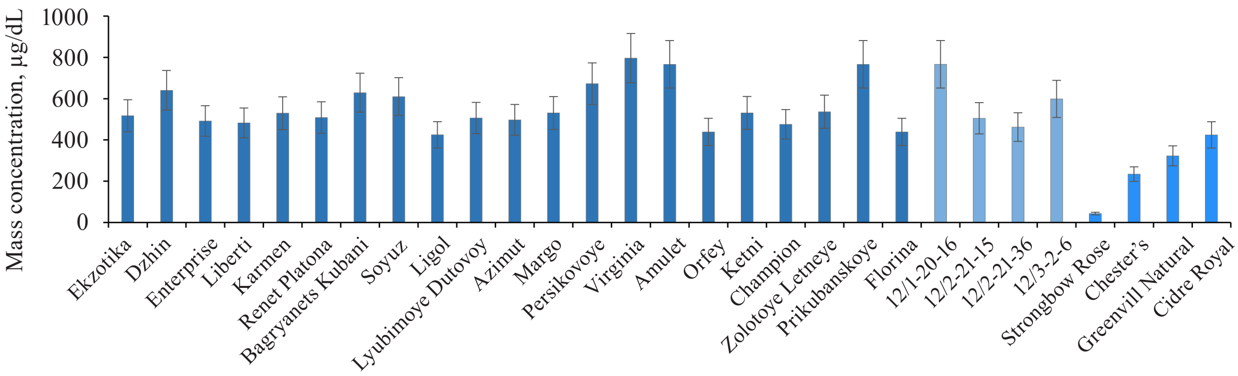

Figure 1 Mass concentrations of iron cations in ciders

from Dzhin, Ekzotika, and Lyubimoye Dutovoy varieties, as well as from the 12/2-21-15 apple tree. Also high were the contents of molybdenum (> 50 µg/L) in the Dzhin ciders; rubidium (> 750 µg/L) in the Virginia, Amulet, and Prikubanskoye ciders; cesium (> 2.5 µg/L) in the Florina, Orfey, Prikubanskoye, Renet Platona, Amulet, and Zolotoye Letneye samples; nickel (> 30 µg/L) in the ciders from Orfey, Virginia, and Enterprise; and titanium (> 2.0 µg/L) in the Prikubanskoye, Ketni, Virginia, Margo, Persikovoye, and Orfey ciders.

Titanium and cesium are often present simultaneously, and their concentrations correlate with each other. This can be explained by the fact that titanium salts have a high sorption capacity for cesium ions, including in soils [22, 23]. Ligands formed by titanium attract cesium ions through electrostatic mechanisms. Our study did not reveal any significant relationships between the concentrations of these cations. Yet, they depended on the varietal characteristics of apples. The highest concentrations of titanium were found in the ciders from Prikubanskoye, Ketni, Orfey, Virginia, and Margo varieties, while cesium was most abundant in the Florina, Prikubanskoye, Orfey, Amulet, and Zolotoye Letneye ciders.

The concentrations of heavy metals or toxic elements are legislatively regulated worldwide. In Russia, they are governed by the Technical Regulations of the Customs Union TR TS 021/2011 [24, 25]. Such microelements are widely used in microfertilizers, but in high concentrations they can disrupt biological cycles, suppress plant growth, and sometimes even cause plants to die. Especially toxic for living organisms are high concentrations of tin, cadmium, copper, zinc, and nickel [26, 27]. Therefore, although microfertilizers are highly effective, they should not exceed the recommended concentrations of heavy metals to prevent them from accumulating in the soil and getting into fruits and their products, including ciders. Excessive amounts of microelements, just as their deficiency, can cause metabolic disorders in the development of apple trees.

It is important to know the concentrations of toxic elements in cider not only to assess potential health risks, but also to evaluate its quality, origin, and authenticity.

In our study, the contents of mercury and arsenic were below the lower limits of the range established by the method we used – none of the samples exceeded their maximum permissible concentrations. Therefore, they are not presented in Table 2. Neither were the conrations of cadmium and lead exceeded in the samples. However, we found statistically significant differences depending on the variety of apples. In particular, the highest concentration of lead (> 20 µg/L) was found in the Soyuz cider, while the highest content of cadmium (10–11 µg/L) was detected in the ciders from Champion, Virginia, Liberti, and Ligol varieties.

The commercial samples had somewhat lower concentrations of cadmium and lead than the experimental samples, which is associated (just as with other elements) with their exposure to various technological treatments.

The experimental ciders were evaluated for their sensory characteristics (Table 3). All the samples had clean aroma and taste without any off-flavors. Some of the samples made from fresh must were opalescent, since they were not additionally clarified. The ciders only clarified by settling, followed by sediment separation and

Table 3 Sensory evaluation of ciders

No.	Name of sample	Sensory characteristics
		Varietal ciders from different pomological varieties of apples
1	Ekzotika	Transparent, of a golden color with a greenish tint. Bright aroma with tones of exotic fruits, green apple, and quince. Fresh and clean taste.
2	Dzhin	Opalescent, of a golden color. Bright aroma with tones of fresh apple and dried fruit. Full taste with cream-cheese hints.
3	Enterprise	Transparent, of a golden yellow color. Complex aroma with tones of apple, banana, and mango. Full, tannic taste.
4	Liberti	Opalescent, of a golden color. Bright aroma with tones of peach, pineapple, and mango. Full taste with cream-cheese hints.
5	Karmen	Opalescent, of a golden-orange color. Bright aroma with tones of fruit stones, dried fruits, and citrus fruits. Fresh, full, tannic taste.
6	Renet Platona	Opalescent, of a golden-brown color. Complex aroma with tones of honey, flowers, and citrus fruits. Full, tart, fresh taste.
7	Bagryanets Kubani	Opalescent, of a straw-golden color. Bright aroma with tones of green apple and citrus fruits. Fresh, full taste with creamy tones in the aftertaste.
8	Soyuz	Opalescent, of a golden-brown color. Clean aroma with tones of fresh apple, caramel, and dried fruit. Full, tannic taste.
9	Ligol	Opalescent, of a straw color. Complex aroma with tones of berries, apples, dried fruits, and flowers. Full, harmonious taste.
10	Margo	Transparent, of a golden color. Bright aroma with floral and fruity tones. Clean, fresh, and full taste.
11	Persikovoye	Opalescent, of a golden-orange color. Complex aroma with tones of plum, cherry plum, peach, and caramel. Full and fresh taste.
12	Virginia	Opalescent, of a golden-orange color. Complex aroma with dried fruit hints. Full, tart, and fresh taste.
13	Amulet	Opalescent, of a golden-brown color. Complex aroma with tones of fresh and baked apple. Full, fresh taste with tones of dried fruits.

Continuation of Table 3

No.	Name of sample	Sensory characteristics
		Varietal ciders from different pomological varieties of apples
14	Orfey	Transparent, of a straw color. Clean, bright aroma with hints of green apple and exotic fruits (mango). Clean, full, harmonious taste.
15	Ketni	Opalescent, of an orange-golden color. Clean aroma with tones of dried fruits, banana, and quince. Full, tannic, and tart taste.
16	Champion	Transparent, of a straw-golden color. Fruity aroma with cider (apples and fermentation) tones. Full, tannic, and tart taste.
17	Zolotoye Letneye	Opalescent, of a golden-orange color. Fruity aroma with tones of undergrowth, fresh apple, and dried fruits. Simple, flat taste.
18	Prikubanskoye	Opalescent, of a golden-brown color. Fruity aroma with tones of fresh fruits (apples, pears, quince). Full, fresh taste.
19	Florina	Opalescent, of a bright yellow color. Clean aroma with tones of fresh apple and fruity-floral nuances. Full, tart, slightly bitter taste.
20	Lyubimoye Dutovoy	Opalescent, of a golden color. Clean aroma with tones of fresh apple and dried fruit. Simple taste with low tannins.
21	Azimut	Opalescent, of a golden-orange color. Bright aroma with tones of plum, cherry plum, and citrus. Full, fresh, and tart taste.
		Varietal ciders from various apple tree forms
22	12/1-20-16	Opalescent, of a golden-brown color. Complex aroma with tones of wild rose and dried fruits. Full, fresh, and tart taste
23	12/1-21-36	Opalescent, of an orange-golden color. Complex aroma with tones of rotten foliage and dried fruits. Flat, watery, simple taste with low tannins.
24	12/2-21-15	Opalescent, of a light straw color. Fruity aroma with tones of fresh apple and fruit stones. Full taste with tones of dried fruits.
25	12/3-21-6	Opalescent, of a golden-orange color. Bright aroma with tones of plum, cherry plum, and citrus. Full, fresh, and tart taste.
		Commercial ciders
26	Strongbow Rose	Transparent, of a pink color. Clean, bright, and fruity-floral aroma with tones of apple. Clean and harmonious taste with tones of fermentation.
27	Chester's	Transparent, of a straw color with a greenish tint. Clean aroma with hints of apple and caramel. Fully developed, fresh taste with tones of fermentation.
28	Greenvill Natural	Transparent, of a pink color. Clean aroma with tones of fresh apple. Full, harmonious, rounded taste with well-pronounced tones of fermentation.
29	Cidre Royal	Transparent, of a straw color with a yellow tint. Bright aroma with tones of fresh apple. Full, harmonious, rounded taste with well-pronounced tones of fermentation.

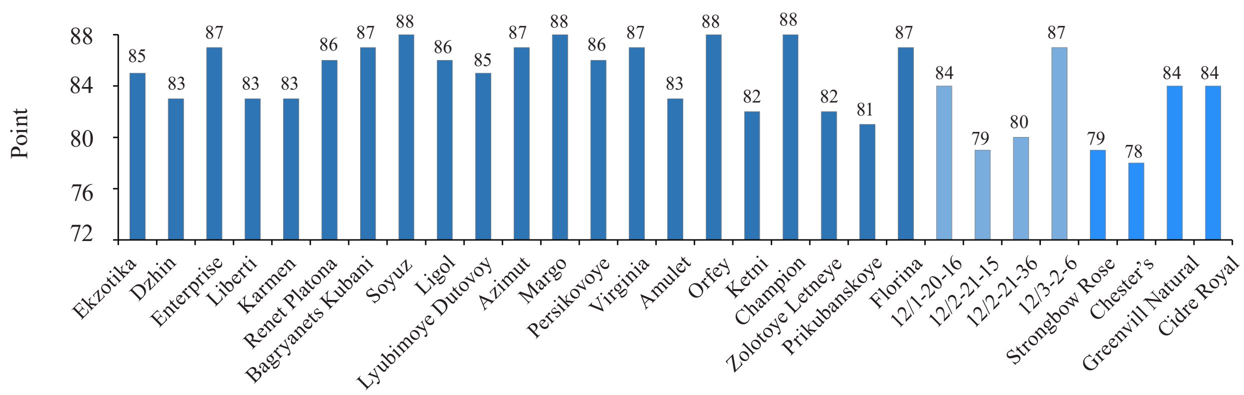

Figure 3 Sensory scores for ciders

filtration through filter sheets. The sensory scores were in the range of 79–88 points (Fig. 3).

The highest sensory scores were given to the experimental ciders from Soyuz, Virginia, Champion, and Prikubanskoye apple varieties (88 points) and the samples from Enterprise, Bagryanets Kubani, Margo, Persikovoye, Orfey, and Azimut varieties, as well as the 12/3-21-6 apple tree (87 points). These ciders had a bright aroma with various hints and a harmonious, full taste. The commercial samples received 78–84 points. They had a clean apple aroma and a taste with pronounced fermentation tones.

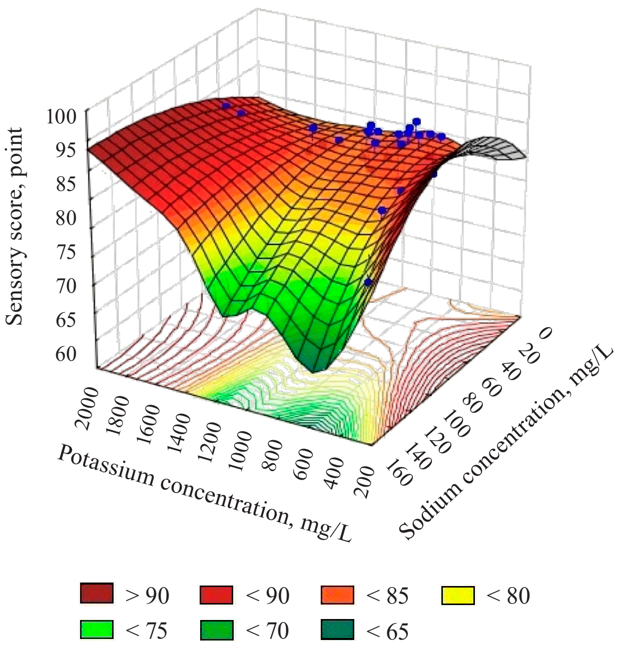

Figure 4 Effect of potassium and sodium cations on the sensory evaluation of ciders

The experimental data were statistically processed to establish a relationship between the concentrations of macroelements in the ciders and their sensory scores. As a result, we found a statistically significant positive relationship between the potassium content ($r = 0.4$) and the sensory score, as well as a negative relationship between the sodium content ($r = –0.4$) and the sensory score. The highest scores were given to the cider samples with potassium ranging from 850 to 1900 mg/L and sodium ranging from 100 to 10 mg/L (Fig. 4).

CONCLUSION

Thus, we found significant differences in the concentrations of all metal cations depending on the pomological variety of apples. If the varieties under study were grown in different soils and climatic conditions, with the use of different fertilizers and crop protection products, we might assume that the differences in the elemental composition of the ciders were down to the growing conditions, agricultural practices, and other technogenic and anthropogenic factors. However, the varieties we used were grown under the same agrotechnical conditions. Therefore, we concluded that the differences in the elemental profile of the ciders were determined by the genetic characteristics of the respective varieties. As a result, we constructed the following elemental profiles of the ciders depending on the concentration of metal cations: K > Na > Ca = Mg > Fe for macronutrients and Rb > Cu > Mn = Zn > Ni > Cs > Ti for microelements.

The commercial samples of ciders, especially those obtained from directly extracted juice, had similar concentrations of copper to those in the experimental ciders and much lower concentrations of other microelements. The cider made from concentrated apple juice did not contain any manganese, molybdenum, or nickel, and its concentration of rubidium was 5–8 times lower than in the ciders made from fresh juice. The revealed concentrations of microelement cations provide information on the relationship between the cider and the composition of the soil on which the apple trees were grown. Therefore, they can be used as a marker of the origin of the beverage.

CONTRIBUTION

N.M. Ageyeva and E.V. Ulyanovskaya developed the research concept and design. A.A. Khrapov and E.A. Chernutskaya collected and analyzed the material. N.M. Ageyeva, A.A. Shirshova, and E.V. Ulyanovskaya wrote and edited the manuscript. L.E. Chemisova processed the data statistically; and all the authors approved the final version of the article.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding this publication.

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