

Features of the results of conductometric studies of apple juices

Svetlana Nikulina^{1*}, *Natalia Fateeva*², *Evgenia Cherekanova*², *Tatiana Verizhnikova*²,
*Ekaterina Smirnova*³, *Alexander Vasyukov*³, and *Irina Nazarova*³

¹Federal State Autonomous Educational Institution of Higher Education "Patrice Lumumba Peoples' Friendship University of Russia", Moscow, Russia

²Kaluzhsky Branch of the Federal State Budgetary Educational Institution of Higher Education "Bauman Moscow State Technical University (National Research University)" (KF Bauman Moscow State Technical University), Kaluga, Russia

³Federal State Budgetary Educational Institution of Higher Professional Education "Kaluga State University named after K.E. Tsiolkovsky", Kaluga, Russia

Abstract. By the conductometric method, the dependence of the specific electrical conductivity (χ) of five apple juice samples on the volume fraction (φ) of apple juice in a solution with distilled water. The dependence χ in the range φ from 0 to 1 acquires a power-law character (the correlation coefficient is close to 1), since a significant part of the mineral composition of apple juices consists of various organic acids. The technique fully complies with the principles of "green" chemistry, since the "waste" is apple juice diluted with distilled water.

1 Introduction

Currently, the consumption of juices of domestic production is growing rapidly. The increase in the number of producers and the variety of juices, along with the weakening of the national quality control system, has led to a decrease in the quality and safety of juice products. Therefore, the falsification of natural juices and juice-containing beverages is a serious problem. It is no coincidence that a lot of documents are devoted to the identification of juice products, among which GOST 34460- 2018 should be highlighted [1].

In this document, the identification of juice products is carried out in accordance with the approved list of physico-chemical indicators, the characteristics of which are determined by various analytical methods. Such indicators include: mass fraction of soluble solids in juices; mass fraction of sediment; volume fraction of pulp; mass fraction of carbon dioxide; mass fraction of preservatives; mass fraction of dyes; mass fraction of sweeteners [1, 2]. There is no conductometry among the proposed analytical methods.

One of the most common forms of adulteration of natural juices is diluting them with water. To identify and detect such falsification of juice products, methods are recommended, each of which has its advantages and disadvantages. The most

* Corresponding author: tanya.chud@ya.ru

environmentally friendly method for assessing changes in the mineral composition of aqueous solutions is the conductometric method [3, 4], the use of which has not found wide application in the chemical analysis of juice products.

The aim of the work is to conduct conductometric studies of the mineral composition of various samples of direct-pressed apple juice and to establish quantitative characteristics of the dependence of the specific electrical conductivity (χ) of direct-pressed apple juice on the degree of its dilution with distilled water.

The scientific novelty of the work is that the nonlinear dependences of apple juice on the degree of their dilution with distilled water are established.

Practical value – the methodology for identifying apple juice when it is diluted by the conductometric method has been expanded.

2 Methodology and objects of research

The objects of research were five samples of natural juices. Conventionally, they received the designations: sample No. 1, sample No. 2, sample No. 3, sample No. 4 and sample No. 5.

The first two juices, samples No. 1 and sample No. 2, were prepared from ripe apples of the "Shtrifel" and "Victory Day" varieties, respectively, using an electric juicer. To prepare apple juice, 2.5 kg of ripe apples were taken. The volume of juice that turned out was for sample No. 1 – 1 l, for sample No. 2 – 0.75 l.

Sample No. 3 - direct-pressed pasteurized apple juice "Vkusvill" (IP head of the farm Chikobava K. A., 412751, Russian Federation, Saratov region, Khvalynsky district, Podlesnoye village, Sadovaya str., 76.).

Sample No. 3 - direct-pressed apple juice, clarified "Gardens of the Don Region" (JSC "Gardens of Pridonya", Russia, 403027, Volgograd region, Gorodishchensky district, village. Gardens of the Don region.)

Sample No. 3 - direct-pressed apple juice "Lenta" (LLC "NAR", Russia, 188561, Leningrad region, Slantsy, Tchaikovsky str., house 7A).

According to literature data, carbohydrates predominate in the composition of apple juice, the content of which can be more than 100 g in 1 liter of juice [6]. At the same time, potassium ions predominate among the cations – the content of which is about 1 g / l. Based on the above, it can be concluded that the mineral composition of apple juice is represented by a wide range of organic compounds with a small part of inorganic substances. All this can significantly affect the dependence of juices when they are diluted with distilled water. Therefore, two variants of the study of the dependence of the investigated solution on the volume fraction of juice were chosen.

Option 1. The dependence of the model solution on the volume fraction of the studied juice in the range φ from 0 to 50% was investigated. 40 ml of distilled water was measured. Next, 40 ml of the studied juice was added to this volume from a burette (pipette) in portions of 1.0 or 5.0 ml and the χ of the resulting solution was measured after 1 minute of intensive mixing of the solution using a magnetic stirrer.

Option 2. The dependence of the model solution on the volume fraction of the studied juice in the range φ from 100 to 50% was investigated. 40 ml aliquots of the studied juice were measured. 40 ml of distilled water from a burette (pipette) was added to this aliquot in portions of 1.0 or 5.0 ml and further studies are carried out similarly to option 1.

The measurements were carried out using a conductometer– an Anion 4100 series laboratory liquid analyzer model A4155. The operability of the measuring channels was checked according to the operating manual [7] during the execution of the current

definitions of the comparison and analysis of the measurement results of distilled water and standard KCl solutions.

Standard solutions of KCl (GOST 4234-77, h.h.) were prepared from fixanal. Distilled water was used according to GOST 6709-72 [8] with χ 5·mcm/cm.

3 Results and their discussion

Table 1 shows the results of measuring χ of the studied apple juice (sample No. 1) when it is diluted with distilled water. The titration sequence of the studied juice with distilled water was carried out according to option 2.

Table 1. Dependence of χ apple juice (analyzed solution) on its ϕ in the test solution when diluting distilled water (25 °C).

Aliquot	Volume fraction of the test solution (ϕ , %) and χ of the solution (mcm/cm)										
	1.00	0.976	0.930	0.889	0.800	0.727	0.667	0.615	0.571	0.533	0.50
1	2260	2234	2177	2123	1988	1875	1772	1681	1600	1526	1458
2	2233	2221	2162	2106	1970	1860	1750	1662	1581	1505	1438
3	2276	2251	2194	2128	2010	1882	1785	1692	1601	1542	1494
4	2247	2231	2170	2123	1990	1876	1768	1686	1609	1538	1454
5	2251	2237	2177	2123	2002	1882	1770	1692	1605	1532	1467
χ Sec.	2254	2234	2176	2120	1989	1873	1769	1680	1598	1528	1461
Sr,	11.5	7.5	8.1	5.9	11.2	6.1	7.8	8.8	7.3	10.5	14.7
Sr, %	0.5	0.3	0.4	0.3	0.6	0.3	0.4	0.5	0.5	0.7	1.0

As follows from the obtained statistically processed experimental data, the average value of χ for sample No. 1 decreases from 2254 mcm/cm to 1461 mcm/cm when the study is diluted with distilled water twice. It should be noted that the standard deviation (Sr) at $n = 5$ does not exceed 1%. This indicates a rather small error of the conductometric method, which is consistent with the literature data.

For samples No. 2, No. 3, No. 4, No. 5 the results of similar studies from their volume fraction of the injected distilled water solution (25 °C) are presented in Table 2.

Table 2. Dependence of the average value of χ apple juice for samples No. 2, No. 3, No. 4, No. 5 of their volume fraction of the introduced distilled water solution ($n = 5$, 25 °C).

Aliquot	Volume fraction of the test solution (ϕ , %) and χ of the solution (mcm/cm)										
	1.00	0.976	0.930	0.889	0.800	0.727	0.667	0.615	0.571	0.533	0.50
Sample No. 2											
χ Sec.	1897	1882	1840	1797	1690	1596	1514	1437	1371	1313	1269
Sr,	9.2	11	7.9	9.3	8.9	9.3	7.6	7.6	7.1	14	9.8
Sr, %	0.5	0.6	0.4	0.5	0.5	0.6	0.5	0.5	0.5	1.1	0.8
Sample No. 3											
χ Sec.	2359	2330	2270	2215	2082	1962	1855	1761	1687	1621	1567
Sr,	19	20	19	17	19	18	19	16	14	34	33
Sr, %	0.8	0.8	0.8	0.7	0.9	0.9	1.0	0.9	0.8	2.1	2.1
Sample No. 4											
χ Sec.	2209	2195	2157	2105	1979	1863	1761	1663	1579	1502	1434
Sr,	3.8	5.4	9.8	9.5	13	10	9.0	9.7	9.3	8.6	8.3
Sr, %	0.2	0.3	0.5	0.5	0.6	0.6	0.5	0.6	0.6	0.6	0.6
Sample No. 5											
χ Sec.	1789	1773	1728	1675	1566	1473	1391	1328	1254	1208	1141
Sr,	6.1	8.0	5.8	7.6	6.5	6.3	4.8	17	3.7	11	3.8
Sr, %	0.3	0.5	0.4	0.4	0.4	0.4	0.3	1.3	0.3	0.9	0.4

As follows from the data presented, for sample No. 2, the value of χ when diluting the test solution is halved from 1897 mcm/cm to 1269 mcm/cm, for sample No. 3 - from 2359 mcm/cm to 1567 mcm/cm, for sample No. 4 – from 2209 mcm/cm to 1434 mcm/cm, and for sample No. 5 - from 1789 mcm/cm to 1141 mcm/cm.

Conditionally, according to the initial value of χ , the studied solutions can be divided into two groups. The first group (sample No. 2 and No. 5) have values of χ less than 2000 mcm/cm, on average 1800 mcm/cm. The second group (samples No. 1, No. 3, No. 4) have a higher value of χ in the range of 2200- 2400 mcm/cm. Thus, these two groups differ in the value of the UE by almost 500 microns/cm.

Everyone knows that because of the fermentation process of various juices, including apple, wine drinks are formed. Earlier conductometric studies have shown that the dependence of χ on the volume fraction of a wine drink when it is diluted with distilled water has a linear character with a value of R^2 of at least 0.99.

Using the data in Tables 1 and 2 for each of the five studied apple juices, a graph of the dependence of the studied solution on its volume fraction was constructed. An example of such a graph for sample No. 1 is shown in Figure 1.

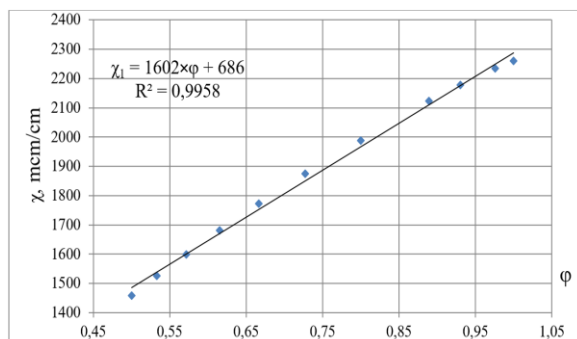


Fig. 1. Dependence of the investigated solution (sample No. 1) on its volume fraction in the solution.

As can be seen from the data presented in the figure, the dependence of the investigated solution (sample No. 1) on its ϕ in solution is linear, while the correlation coefficient is close to 1. The tangent of the slope angle of this dependence is conventionally fashionable to call the identification coefficient [4, 5].

For samples No. 1, No. 2, No. 3, No. 4, No. 5 similar dependences were constructed, which also have a linear character in the investigated range ϕ .

Table 3 summarizes the results of statistical data processing of the dependence χ (mcm/cm) on the juice ϕ in the test solution from $\phi=1.0$ to $\phi=0.5$. The S_r of the results obtained ranges from 0.3 to 1.2%, which confirms the literature data on a small error (ranging from 1-2%) of conductometric measurements.

Table 3. Dependence of the average value of χ apple juice for samples No. 2, No. 3, No. 4, No. 5 of their volume fraction of the introduced distilled water solution ($n= 5, 25^\circ\text{C}$).

Indicator	Sample No. 1	Sample No. 2	Sample No. 3	Sample No. 4	Sample No. 5
	$\phi=0.5-1.0$				
$K_{ind} \pm S_r$	1592 ± 11	1282 ± 16	1569 ± 10	1569 ± 10	1287 ± 14
$S_r, \%$	0.7	1.2	0.3	0.6	1.1
	$\phi=0.0-0.5$				
$K_{ind} \pm S_r$	2652 ± 5	2265 ± 6	2892 ± 26	2702 ± 19	2159 ± 10
$S_r, \%$	0.2	0.3	0.9	0.7	0.5

A comparison of the average values of K_{ind} shows that two groups of juices can be distinguished by this indicator. The first group includes sample No. 1, No. 3, No. 4, for which K_{ind} has similar values and are respectively equal (1592 ± 11) , (1614 ± 60) and (1569 ± 10) mcm/cm. The second group, this sample No. 2 and No. 5 have respectively (1282 ± 16) and (1287 ± 14) mcm/cm.

The division of the studied juices into two groups, which differ significantly in the value of K_{ind} by more than 300 microns / cm, indicates the possible use of K_{ind} to assess the mineral composition of juices, which, as a rule, is individual depending on the geomorphological and climatic conditions of the area where the apple harvest was formed.

Figure 2 shows all five dependences of the studied solutions on the apple juice in solution.

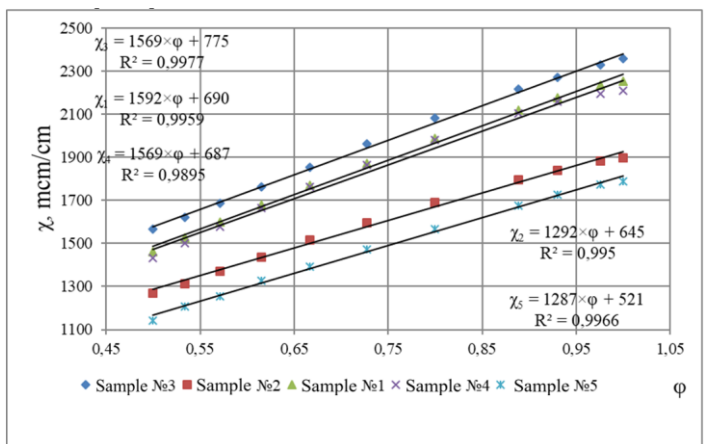


Fig. 2. The dependence of the studied solutions of five samples of apple juice on the ϕ of apple juice in solution.

The obtained dependencies are linear in nature, which is confirmed by all five values of the correlation coefficient, which are very close to 1. It should be noted that all five obtained dependencies, although linear in nature, do not pass through the origin. This feature may be a consequence of the influence of the ionic force on the values of.

Table 4 shows the results of measuring distilled water when apple juice is injected into it (sample No. 1). The titration sequence with distilled water with the juice under study was carried out according to option 1.

Table 4. Dependence of χ distilled water (analyzed solution) on ϕ injected apple juice solution No. 1 (25 °C).

Aliquot	Volume fraction of the test solution (ϕ , %) and χ of the solution (mcm/cm)										
	0.00	0.02	0.07	0.11	0.20	0.27	0.33	0.38	0.43	0.47	0.50
1	26	195	338	475	727	941	1086	1203	1304	1385	1453
2	43	174	353	476	726	936	1084	1201	1300	1384	1455
3	25	187	347	476	727	943	1092	1212	1311	1392	1457
4	21	181	353	487	722	941	1091	1202	1303	1390	1452
5	43	168	346	479	720	935	1082	1201	1296	1368	1450
$\chi_{Avg.}$	29	184	348	478	726	940	1088	1204	1305	1388	1454
S_{r2}	1.19	7.94	4.46	3.56	2.74	3.05	3.65	3.35	3.63	6.24	2.02
$Sr, \%$	3.2	4.31	1.28	0.74	0.38	0.32	0.34	0.28	0.28	0.45	0.14

As follows from the experimental data obtained, after statistical processing, the average value of χ for sample No. 1 increases from 29 mcm/cm to 1454 mcm/cm when apple juice is added to distilled water. At the same time, it should be noted that Sr at $n = 5$ with the first two additions of juice fluctuates at the level of 3-4%, and with subsequent additions of apple juice does not exceed 1%. This indicates a rather small error of the conductometric method, which is consistent with the literature data.

For samples No. 2, No. 3, No. 4, No. 5 The results of similar studies from their injected apple juice solution (25 °C) are presented in Table 5.

Table 5. Dependence of χ distilled water (analyzed solution) on ϕ injected apple juice solution No. 2 (25 °C).

Aliquot	Volume fraction of the test solution (ϕ , %) and χ of the solution (mcm/cm)										
	0.00	0.02	0.07	0.11	0.20	0.27	0.33	0.38	0.43	0.47	0.50
Sample No. 2											
$\chi_{Avg.}$	37	161	311	424	641	796	943	1040	1123	1195	1254
S_{r_s}	7.7	1.2	7.9	3.4	2.0	3.0	0.6	3.9	2.2	2.7	1.8
$S_{r_s} \%$	2.1	0.8	2.5	0.8	0.3	0.4	0.1	0.4	0.2	0.2	0.1
Sample No. 3											
$\chi_{Avg.}$	29	160	332	476	752	983	1147	1274	1384	1470	1546
S_{r_s}	1.1	8.2	13.5	6.4	4.2	3.9	4.1	4.1	4.4	5.0	6.6
$S_{r_s} \%$	3.5	5.1	4.1	1.3	0.6	0.4	0.3	0.3	0.3	0.3	0.4
Sample No. 4											
$\chi_{Avg.}$	4	142	296	421	694	905	1049	1172	1279	1367	1439
S_{r_s}	0.13	2.0	8.5	3.5	5.1	6.0	10.3	8.5	7.7	16.0	14.7
$S_{r_s} \%$	3.2	1.4	2.8	0.8	0.7	0.7	0.9	0.7	0.6	1.1	1.0
Sample No. 5											
$\chi_{C_{peil}}$	3	113	231	330	527	685	828	927	1012	1083	1138
S_{r_s}	0.03	3.5	1.6	8.2	15	3.6	4.9	9.0	6.6	4.9	8.2
$S_{r_s} \%$	0.9	3.1	0.7	2.5	3.0	0.5	0.6	0.9	0.6	0.5	0.7

As follows from the data presented, for sample No. 2, the value of χ when diluting the test solution is doubled from 37 mcm/cm to 1254 mcm/cm, for sample No. 3 - from 29 mcm/cm to 1546 mcm/cm, for sample No. 4 - from 4 mcm/cm to 1439 mcm/cm, and for sample No. 5 - from 3 mcm/cm to 1138 mcm/cm. Conditionally, according to the initial value of χ , the studied solutions can be divided into two groups. The first group (sample No. 2 and No. 5) have an average of 1200 microns/cm. The second group (samples No. 1, No. 3, No. 4) have a higher value of χ in the range of 1439 - 1546 mcm/cm. Thus, these two groups differ in the value of χ by almost 300 microns/cm.

Using the data in Tables 4 and 5 for each of the five studied apple juices, a graph of the dependence of the studied solution on its ϕ was constructed. An example of such a graph for sample No. 1 is shown in Figure 3.

As can be seen from the data presented in the figure, the dependence of the investigated solution (sample No. 1) on its ϕ in solution is linear, while the correlation coefficient is close to 1.

For samples No. 2, No. 3, No. 4, No. 5 similar dependences were constructed, which also have a linear character in the investigated range ϕ .

Table 6 summarizes the results of statistical processing of the data of the dependence χ (mcm/cm) on the juice ϕ in the test solution from 0 to 0.5. The Sr of the results obtained ranges from 0.2 to 0.9%, which confirms the literature data on a small error (ranging from 1-2%) of conductometric measurements.

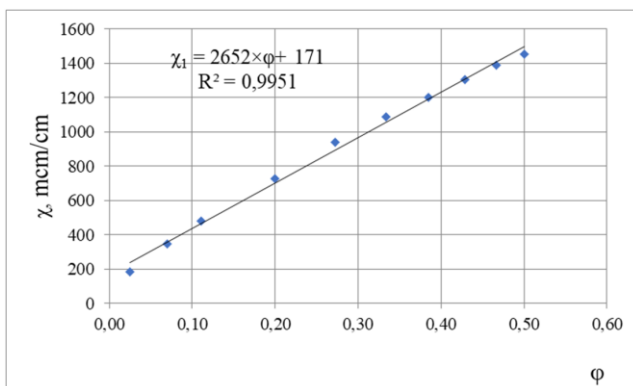


Fig. 3. Dependence of the investigated solution (sample No. 1) on its ϕ in solution.

A comparison of the average values of K_{ind} shows that two groups of juices can be distinguished by this indicator. The first group includes sample No. 1, No. 3, No. 4, for which K_{ind} has similar values and are respectively equal (2652 ± 5) , (2892 ± 26) and (2702 ± 19) mcm/cm. The second group, this sample No. 2 and No. 5 have respectively (2265 ± 6) and (2159 ± 10) mcm/cm.

The division of the studied juices into two groups, which differ significantly in the value of K_{ind} by more than 400 microns / cm, indicates the possible use of K_{ind} to assess the mineral composition of juices, which, as a rule, is individual depending on the geomorphological and climatic conditions of the area where the apples were harvested.

Figure 4 shows all five dependences of the studied solutions on the apple juice in solution.

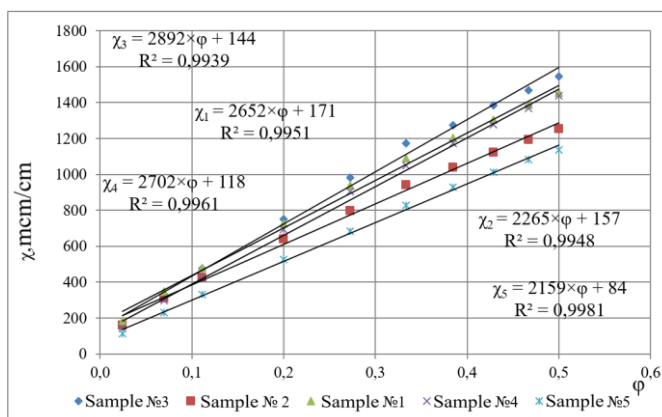


Fig. 4. The dependence of the studied solutions of five apple juice samples on the ϕ of apple juice in solution in the range from 0 to 0.5.

The obtained dependencies are linear in nature, which is confirmed by all five values of the correlation coefficient, which are very close to 1. It should be noted that all five obtained dependencies, although linear in nature, do not pass through the origin. This feature may be a consequence of the influence of the ionic force on the values of.

Thus, considering separately the dependence of the studied solutions of five juice samples on the ϕ of apple juice in solution in the range from 0 to 0.5 and from 0.5 to 1 shows that this dependence is very close to linear. At the same time, when combining the obtained values and constructing the dependence χ on ϕ in the range from 0 to 1, it gives

grounds to talk about the nonlinearity of this dependence. This can be said on the basis of the correlation values, which fluctuate around 0.97 for all five samples of apple juice studied (Figure 5).

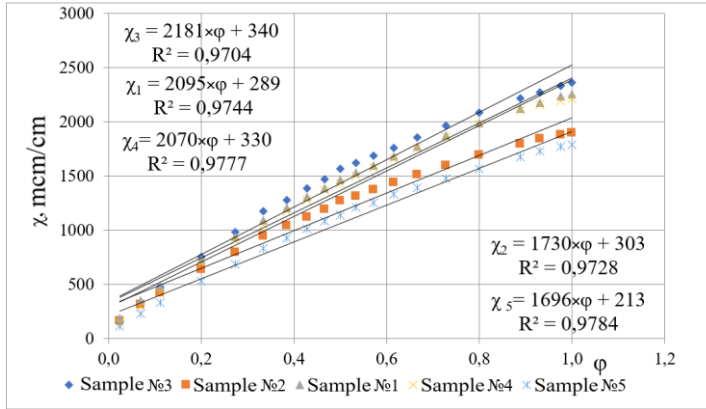


Fig. 5. Linear dependence of the studied solutions of five apple juice samples on the ϕ of apple juice in solution in the range from 0 to 1.

Statistical processing of the dependence χ on ϕ in the range from 0 to 1 shows that the correlation coefficient has the greatest values in the case of the power dependence χ of the studied solutions on ϕ . In this case, the correlation values are very close to 1 (Figure 6).

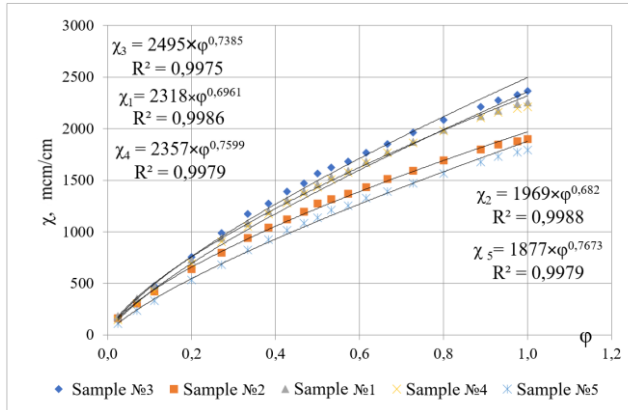


Fig. 6. Linear dependence of the studied solutions of five apple juice samples on the ϕ of apple juice in solution in the range from 0 to 1.

4 Conclusions

Thus, based on the results obtained, the following can be noted.

Statistical processing of the obtained results shows that the dependence of the studied solutions of five juice samples on the ϕ of apple juice in solution in the range from 0 to 0.5 and from 0.5 to 1 is very close to linear (correlation coefficient of at least 0.99).

According to the value of K_{ind} , the studied apple juice samples can be divided into two groups, which differ significantly in the value of K_{ind} by more than 300 microns /cm with a

change in ϕ from 0 to 0.5 and by more than 400 microns / cm with a change in ϕ from 1 to 0.5. This difference can be used to identify apple juices by the Kind value .

When combining the obtained values and constructing the dependence χ on ϕ in the range from 0 to 1, the linear nature of the dependence is significantly distorted, since the value of the correlation coefficient decreases to 0.97, and the dependence acquires a power-law character (the correlation coefficient is close to 1).

The nonlinear nature of the dependence of the studied solutions on the apple juice can be explained by the fact that a significant part of the mineral composition of apple juice consists of various organic acids, so it is no coincidence that the method of potentiometric titration with an alkali solution is used to estimate the amount of these acids.

References

1. *GOST 34460- 2018 Juice products. Identification. General provisions*, Gosstandart of Russia (2019)
2. N.V. Makarova, D.F. Valiulina, *Beer and beverages*, Comparative analysis of physico-chemical properties and antioxidant activity of apple juices, **5** (2012)
3. A.E. Vasyukov, A.P. Korzhavyi, S.N. Nikulina, *Static and dynamic approach to estimation of spring water mineralization stability as a factor of groundwater ecological safety*, Journal of Physics: Conference Series, **1399** (2019)
4. A. Vasyukov, V. Loboichenko, S. Bushtec, *Ecology, Environment and Conservation*, Identification of bottled natural waters by using direct conductometry, **22, 3** (2016)
5. S.N. Nikulina, T.A. Chudakova, K.K. Surinova, E.A. Larionov, E.A. Cherikanova, A.E. Vasyukov, *Ecology and industry of Russia*, Environmentally friendly conductometric technique for monitoring the stability of the mineral composition of spring waters, **25, 4** (2021)
6. L.Ch. Burak, V.V. Yablonskaya, *International Journal of Applied Sciences and Technologies "Integral"*, The influence of the chemical composition and microflora of raw materials on the fermentation process of apple juice, **3** (2021)
7. *Operation manual INFA.421522.002. RE*, Anion 4100 series laboratory liquid analyzers, LLC NPP "Infrapak-Analyte", Novosibirsk (2011)
8. *GOST 6709-72, Distilled water, Technical conditions, Introduction* (1974)