Total concentration of main components in solutions for metal electroplating as a criterion for classifying and choosing resource-saving compositions of solutions

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Total Concentration of Main Components in Solutions for Metal Electroplating as a Criterion for Classifying and Choosing Resource-Saving Compositions of Solutions

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Abstract—A comparative analysis is performed of the variations in the total concentration of the main components $\left(\sum_i c_i\right)$, in the solutions proposed and used in different years for electroplating individual metals (Cr, Cu, Ni, Zn, Sn, Cd, Pb, and Fe). A quantitative concentration criterion is determined for classifying solutions into resource-saving ($\sum_i c_i \le 2.32$ mol-equiv/L) and resource-intensive ($\sum_i c_i \ge 2.78$ mol-equiv/L) compositions. In addition to scientific interest, this material can be useful for developing studies aimed at reducing the negative environmental impact of electroplating shops or sections.

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INTRODUCTION

One of the major areas in the development of modern technologies is a decrease in the resource intensity of production, in particular metal electroplating from aqueous solutions [1]. Previously, in [2], based on a comparative statistical analysis of the ion concentrations of the electrodeposited metal, we obtained a corresponding concentration criterion for classifying the compositions of solutions into resource-intensive, ordinary, and resource-saving compositions. In addition to the compounds of electrodeposited metals, the compositions of solutions include various substances intended for increasing conductivity, improving the dissipating ability of a solution, maintaining the pH level, etc. Surfactants, brighteners, levelers, and other additives are also added to solutions for metal electrodeposition.

In electrodeposition, resource conservation can be achieved not only by optimizing the concentration of the electrodeposited metal in a solution [2, 3], but also by decreasing the amount and concentration of the used chemical compounds, as a consequence of which decreases are observed in the volume of rinsing and waste water; the amount of contaminants in water; and, accordingly, expenditures for water purification.

The aim of this study is to develop a quantitative criterion for classifying solutions into groups of resource-saving and resource-intensive compositions based on the value of the total concentration of the main components in solutions without taking into account various additives (as a rule, organic compounds). The following objectives were undertaken to achieve this goal:

a comparative analysis of variations in the total concentration of the main components in solutions proposed and used in different years for metal electrodeposition (Cr, Cu, Ni, Zn, Sn, Cd, Pb, and Fe);

an analysis of the development of resource conservation during electrodeposition.

PROCEDURE FOR PROCESSING RESULTS

Information on the compositions of solutions that was published in the scientific literature and the catalogs of present-day companies was considered to be experimental data. When forming samples, we considered information on the compositions of solutions developed before 1952 [4] (sample is designated as 1952) and 1984 [5] (sample is designated as 1984), as well as modern developments (up to 2011–2012) offered by a number of companies (according to the following Internet resources: www.bestgalvanik.ru, www.ecomet.ru, www.galvanik.ru, and www.galvanotech.nnov.ru) (sample is designated as 2011). Only the compositions of solutions based on salts or acids that do not contain complex compounds were included in the samples. If the total concentration of components had interval estimation, the minimum and maximum

Table 1. Total concentration of the main components ($\sum_i c_i$, mol-equiv/L) in technological solutions for metal electroplating in 1952, 1984, and 2011 samples for various processes

Metal	$\sum_i c_i$, mol-equiv/L		
	"1952"	"1984"	"2011"
Zn	1.90; 2.08; 2.23; 3.27; 3.75; 3.89	1.91; 2.16; 2.28; 2.33; 2.41; 2.46; 2.51; 3.07; 3.15; 3.16; 3.20; 3.25; 4.17	1.04; 1.55; 1.66; 2.01; 2.03; 2.87; 3.51; 3.54; 3.65; 3.76; 3.79; 4.17; 4.23; 4.44; 4.93; 5.12
Cd	1.25; 1.40; 1.50; 1.62	0.39; 0.59; 0.60; 1.15; 1.22; 1.31; 2.00; 3.06; 3.29; 3.53; 4.00; 4.69; 6.46	–
Cu	2.60; 3.53	2.32; 3.43; 2.26; 2.99; 2.22; 3.43	2.54; 2.55; 2.67; 2.75; 2.99; 3.07; 3.32; 3.40; 3.48
Ni	0.91; 1.00; 1.38; 1.61; 2.08; 2.68; 2.92; 3.01	1.24; 1.50; 1.98; 2.02; 2.34; 2.35; 2.44; 2.58; 2.60; 2.84; 2.90; 2.98; 3.05; 3.12; 3.13; 3.28; 3.30; 3.31; 3.34; 3.53; 3.71; 3.71; 5.88	2.44; 2.46; 2.52; 2.56; 2.60; 2.62; 2.79; 2.88; 2.92; 2.96; 3.09; 3.28; 3.31; 3.37; 3.43; 3.52; 3.89; 4.57
Cr	2.02; 2.55; 3.54; 4.08	1.53; 1.79; 2.24; 2.55; 2.81; 3.06; 5.13; 6.48	0.81; 0.84; 1.31; 1.52; 1.82; 1.86; 2.02; 2.34; 2.55; 2.88
Sn	0.97; 2.54	0.92; 1.17; 1.61; 1.71; 1.87; 2.07; 2.51; 2.54; 3.08; 3.60; 4.20	2.02; 2.38; 3.34; 3.48
Pb	0.97; 1.31; 1.71; 2.00	0.82; 1.37; 1.71; 3.43	–
Fe	–	2.61; 3.61; 3.92; 2.63	–

values were considered to correspond to two independent compositions of solutions.

To compare the concentrations of different compounds contained in solutions and determine the unified quantitative criterion, we used the total concentration of the main components in solutions, which is expressed in mol-equiv/L. The total concentrations of the main components in solutions ($\sum_i c_i$, mol-equiv/L) for samples on each of the electrodeposited metals are given in ascending order in Table 1.

The nonparametric methods of statistical analysis of data [6, 7] were used to reveal differences in the quantitative attribute between the samples, the distribution in which is not known or does not conform to normal distribution, as in solutions for electrodeposition of metals and alloys [3]. These methods are based on hypothesis testing using the nonparametric Mann–Whitney U test. The algorithm of calculations is described in detail in [2].

As before [2, 3], the hypothesis that the experimental distribution density for the total concentration of the main components in solutions corresponds to normal distribution was tested using Pearson's chi-square (χ^2) test. If the calculated value χ^2_{cal} is less than the critical value χ^2_{cr} the experimental data do not contradict the hypothesis of normal distribution. Otherwise, the initial values of the total concentrations of the main components in solutions are transformed so that the distribution of newly obtained values conforms to normal distribution.

To quantitatively characterize the criterion of resource conservation, we used the parametric statistics of normal distribution and the corresponding methods for processing the results, including the determination of the average value, standard deviation, and confidence interval for the average using Student's distribution.

RESULTS AND DISCUSSION

Is the total concentration of the main components in a solution in samples for different metals (Cr, Cu, Ni, Zn, and Sn) in different years approximately the same, or is it different?

Let us formulate the following hypotheses:

–for $\mathbf{H_0}$, in the 1984 and 1952 samples, there are no significant differences between the total concentrations of the main components in solutions for zinc (Cu, Ni, Cr, or Sn) electroplating.

–for $\mathbf{H_1}$, in the 1984 and 1952 samples, there are significant differences between the total concentrations of the main components in solutions for zinc (Cu, Ni, Cr, or Sn) electroplating.

We have formulated similar hypotheses when comparing the 2011 and 1984 samples.

In comparing the 1952 and 1984 samples for zinc, copper, and tin plating, for all of the compared samples, we have $U_{emp} \geq U_{cr}$ (Table 2). Consequently, there is no significant difference between the total concentrations in the samples for these processes (Fig. 1).

Table 2. Results of statistical analysis of samples: sample size, Mann—Whitney test (empirical and critical values), and average value of $\sum_i c_i$ for various metal electroplating processes

Compared samples	"1952" and "1984"	"1984" and "2011"
Zinc plating		
Sample size	6 and 13	13 and 16
Empirical value of the Mann—Whitney test (U_{emp})	39	74,5
Critical value of Mann—Whitney test (U_{cr}) for respective sample size	19	65
Average value of $\sum_i c_i$, mol-equiv/L	2.85 and 2.77	2.77 and 3.27
Copper plating		
Sample size	2 and 6	6 and 9
U_{emp}	9	15,5
U_{cr}	0	12
Average value of $\sum_i c_i$, mol-equiv/L	3.07 and 2.78	2.78 and 3.65
Tin plating		
Sample size	2 and 11	11 and 4
U_{emp}	8.5	29
U_{cr}	1	8
Average value of $\sum_i c_i$, mol-equiv/L	1.76 and 2.30	2.30 and 2.81
Chrome plating		
Sample size	4 and 8	8 and 10
U_{emp}	17.5	17.5
U_{cr}	5	20
Average value of $\sum_i c_i$, mol-equiv/L	3.05 and 3.20	3.20 and 1.80
Nickel plating		
Sample size	8 and 23	23 and 18
U_{emp}	39	233
U_{cr}	55	143
Average value of $\sum_i c_i$, mol-equiv/L	1.95 and 2.92	2.92 and 3.07

For chrome plating solutions, the total concentration of the main components in the 1952 and 1984 samples is statistically indiscernible ($U_{emp} \geq U_{cr}$) (Table 2). In these samples, the weighted average value of $\sum_i c_i$ is 3.13 mol-equiv/L. When comparing the 1984 and 2011 samples, we observe a statistically significant difference in the total concentration of the main components ($U_{emp} \leq U_{cr}$), i.e., the average value of $\sum_i c_i$ decreased from 3.20 to 1.80 mol-equiv/L (Fig. 1).

For nickel plating, we have $U_{emp} < U_{cr}$ (Table 2), which makes it possible to reject hypothesis $\mathbf{H_0}$ and accept hypothesis $\mathbf{H_1}$, which indicates a significant difference between the concentrations in the 1952 and 1984 samples: the average value of the total concentration of the main components in the solution varied

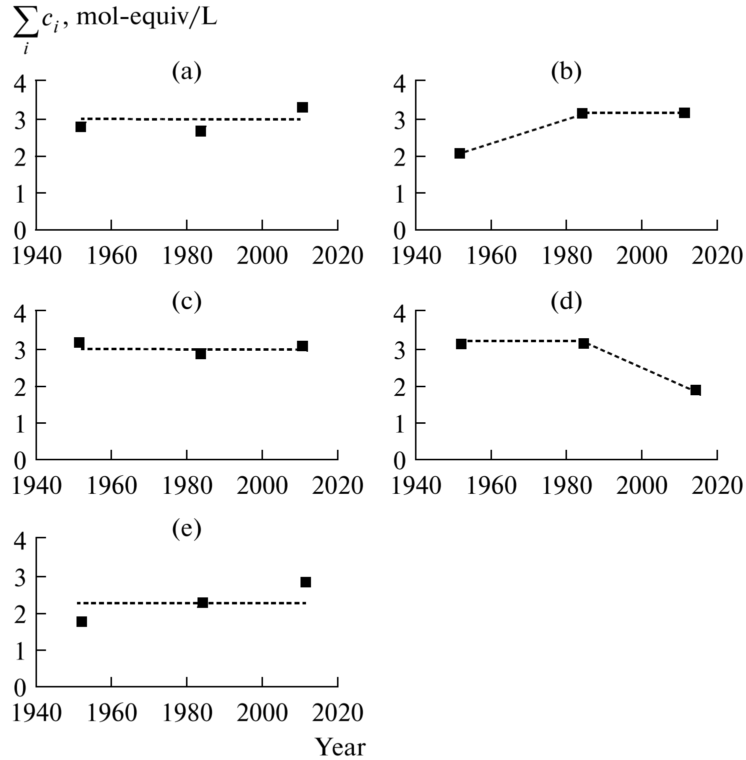

Fig. 1. Average value for total concentration of the main components in solutions proposed and used in different years for metal electroplating: (a) Zn, (b) Ni, (c) Cu, (d) Cr, and (e) Sn.

from 1.95 to 2.92 mol-equiv/L, i.e., it increased by a factor of 1.5 (Fig. 1). In comparing the 1984 and 2011 samples, we have $U_{\text{emp}} > U_{\text{cr}}$; consequently, a significant difference between the concentrations is not observed for this time period, i.e., the weighted average value of $\sum_i c_i$ in the solutions for nickel plating is 3.0 mol-equiv/L.

Thus, in the period of 1984–2011, resource-saving technological solutions (with respect to the total concentration of the main components) were developed and used in industry only for chrome plating. At the same time, the value of $\sum_i c_i$ in solutions for zinc, copper, and tin plating remained unchanged; the weighted average values of $\sum_i c_i$ in solutions for zinc, copper, and tin plating are 3.02, 3.22, and 2.56 mol-equiv/L, respectively, (Fig. 1), which offers further opportunities for developing the resource-saving compositions of solutions. For nickel plating, a considerable increase in the total concentration of components in technological solutions was observed in 1952–1984 and the attained concentration has remained almost unchanged even today.

To determine the bounds of the total concentration of the main components in solutions as a criterion for classifying the compositions of solutions into resource-saving and resource-intensive compositions, we use parametric statistical techniques.

Let us test the sample that combines the 1952, 1984, and 2011 samples for a number of metals (Cr, Cu, Ni, Zn, Sn, Cd, Pb, and Fe) (Table 1) for conformity to the law of normal distribution.

Figure 2a presents the histogram and experimental distribution density for the total concentration of the main components in solutions $\sum_i c_i$. The distribution density for $\sum_i c_i$ has a left-hand asymmetry (the median, modal, and average values of $\sum_i c_i$ are 3.5, 2.5, and 2.72, respectively; the standard deviation is 1.19).

The theoretical curve of normal distribution (Fig. 2a, curve *3*) calculated from these data unsatisfactorily describes experimental data, and the empirical value χ^2_{emp}, = 19.38 is higher than the critical value (χ^2_{cr} (0.05; 4) = 9.5) for a level of significance of 0.05 and four degrees of freedom.

As was shown previously [2], the quantity $\sqrt[3]{\sum_i c_i}$, was used as a new variable, the distribution density of which (Fig. 2b, curves *1*, *2*) has no asymmetry (the median, modal, and average values of $\sqrt[3]{\sum_i c_i}$ are close: 1.3, 1.5, and 1.37, respectively; the standard deviation is 0.21). The curve of normal distribution that is calculated from these data (Fig. 2b, curve *3*) satisfactorily describes the experimental distribution ($\chi^2_{\rm emp}$, = 9.39, which is less than the critical value ($\chi^2_{\rm cr}$ (0.05; 4) = 9.5 for a level of significance of 0.05 and four degrees of freedom).

Table 3 lists the quantitative parameters of the distribution density for $\sqrt[3]{\sum_i c_i}$, and the lower and upper bounds of the variable.

When a sample has a limited size, the point estimation of the average differs from the general average, which can lead to subsequent erroneous inferences. In that case, we use interval estimation, i.e., an interval that includes the true value of the estimated parameter with a given probability. To accomplish this, we construct confidence limits for $\sqrt[3]{\sum_i c_i}$.

The Student confidence interval for $\sqrt[3]{\sum_i c_i}$ has the form

$$\left\langle \sqrt[3]{\sum_i c_i} \right\rangle - \frac{St}{\sqrt{n}} \le \sqrt[3]{\sum_i c_i} \le \left\langle \sqrt[3]{\sum_i c_i} \right\rangle + \frac{St}{\sqrt{n}},$$

where n is the sample size ($n = 165$) and t is Student's n-test. For $n = 165$ and a confidence level of $\alpha = 0.99$, we have $t = 2.6$ [8]; then, $\frac{St}{\sqrt{n}} = \frac{1}{5}S$.

Using the derived characteristics, we distinguish three groups of solution compositions as follows:

(I) resource-saving compositions $\left(\sqrt[3]{\sum_i c_i} \le \left\langle \sqrt[3]{\sum_i c_i} \right\rangle - - \frac{St}{\sqrt{n}}\right)$;

(II) ordinary compositions $\left(\left\langle \sqrt[3]{\sum_i c_i} \right\rangle - \frac{St}{\sqrt{n}} < \sqrt[3]{\sum_i c_i} < \left\langle \sqrt[3]{\sum_i c_i} \right\rangle + \frac{St}{\sqrt{n}}\right)$;

(III) resource-intensive compositions $\left(\sqrt[3]{\sum_i c_i} \ge \left\langle \sqrt[3]{\sum_i c_i} \right\rangle + \frac{St}{\sqrt{n}}\right)$.

The quantitative estimation for all groups according to the chosen criterion, i.e., the total concentration of the main components in solutions for metal electroplating, is given in Table 4.

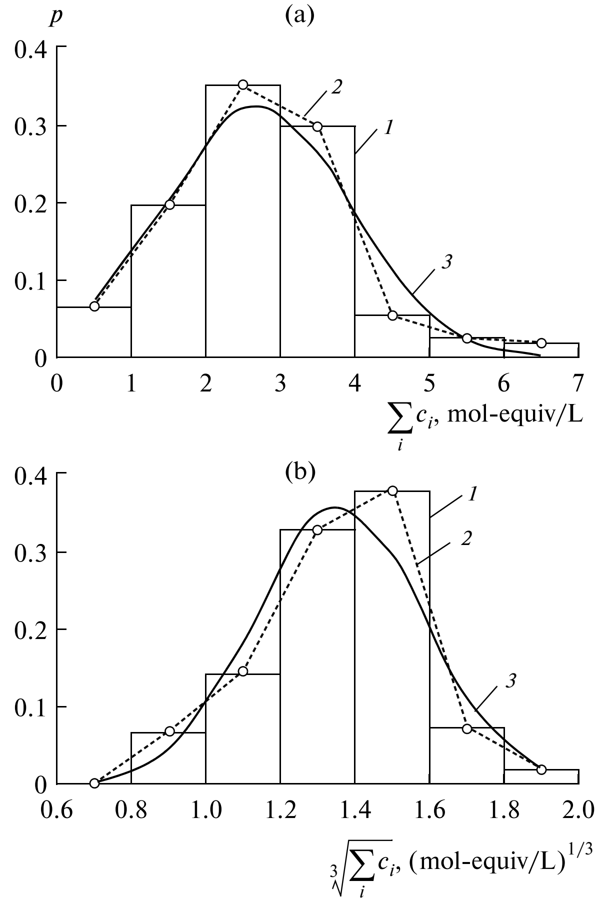

Fig. 2. (*1*) Histogram and (*2*) polygon of relative frequencies of the distribution of variables (a) $\sum_i c_i$ and (b) $\sqrt[3]{\sum_i c_i}$ in solutions for metal electroplating. (*3*) Theoretical curve of normal distribution.

Thus, taking into account the distribution parameters of quantity $\sqrt[3]{\sum_i c_i}$, we determined the bounds of the total concentration of the main components in solutions, i.e., resource-saving ($\sum_i c_i \le 2.32$ mol-equiv/L) and resource-intensive ($\sum_i c_i \ge 2.78$ mol-equiv/L) compositions.

According to these results, the 2011 sample can be classified as follows (Fig. 3): resource-saving compositions (group I) account for 22.8%, ordinary compositions (group II) constitute 21.1%, and resource-intensive compositions (group III) amount to 56.1%.

A considerable fraction of resource-intensive and ordinary solution compositions indicates the expediency of developing and improving the resource-saving

Table 3. Statistical estimates of the distribution parameters of variable $\sqrt[3]{\sum_i c_i}$

Parameters of distribution density	Value
Average value of $\sqrt[3]{\sum_i c_i}$	1.37
Standard deviation S for $\sqrt[3]{\sum_i c_i}$	0.21
Lower bound ($\sqrt[3]{\sum_i c_i} - S$)	1.16
Upper bound ($\sqrt[3]{\sum_i c_i} + S$)	1.58
Lower bound $\sum_i c_{i,\mathrm{L}}$, mol-equiv/L	1.6
Upper bound $\sum_i c_{i,\mathrm{U}}$, mol-equiv/L	3.9

Table 4. Classification for compositions of technological solutions for electroplating (according to $\sum_i c_i$)

Types of compositions of technological solutions for electroplating	Classification indicators	
	$\sqrt[3]{\sum_i c_i}$, (mol-equiv/L)$^{1/3}$	$\sum_i c_i$, mol-equiv/L
Resource-saving compositions (group I)	$\sqrt[3]{\sum_i c_i} \le 1.32$	$\sum_i c_i \le 2.32$
Ordinary compositions (group II)	$1.32 < \sqrt[3]{\sum_i c_i} < 1.41$	$2.32 < \sum_i c_i < 2.78$
Resource-intensive compositions (group III).	$\sqrt[3]{\sum_i c_i} \ge 1.41$	$\sum_i c_i \ge 2.7$

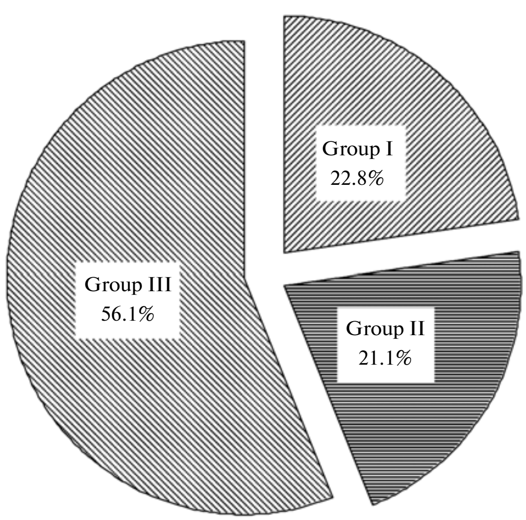

Fig. 3. Diagram classifying the compositions of solutions for metal electroplating into groups according to the total concentration of the main components: (I) resource-saving, (II) ordinary, and (III) resource-intensive compositions of solutions in the 2011 sample.

compositions of solutions by decreasing the total concentration of the main components in solutions.

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NOTATION

$\sum_i c_i$—total concentration of the main components in the technological solution, mol-equiv/L;

$\sum_i c_{i,\mathrm{U}}$—upper bound of the total concentration of the main components in the technological solution, mol-equiv/L;

$\sum_i c_{i,\mathrm{L}}$—lower bound of the total concentration of the main components in the technological solution, mol-equiv/L;

$\left\langle \sqrt[3]{\sum_i c_i} \right\rangle$—average value of the variable $\sqrt[3]{\sum_i c_i}$;
$\mathbf{H}_0$—null hypothesis;
$\mathbf{H}_1$—competing (alternative) hypothesis;
n—sample size;
S—standard deviation, mol-equiv/L;
t—Student t-test;
U—Mann–Whitney test;
U_{cr}—critical value of the Mann–Whitney test;
U_{emp}—empirical value of the Mann–Whitney test;
α—confidence level;
χ^2—Pearson's chi-square test;
χ^2_{cr}—critical value of Pearson's chi-square test;
χ^2_{emp}—empirical value of Pearson's chi-square test.

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