Robust parameter design of the procedure for determining the chemical composition of copper alloys by X-ray fluorescence

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Abstract

The paper offers a brief overview of the modern procedures for determining the chemical composition of copper alloys along with the applied methods of analytical control. It has been shown that to obtain reliable and comparable results of measuring the mass fractions of copper alloys elements within wide ranges of values, the most suitable procedures are based on the X-ray fluorescence method, implemented using portable X-ray fluorescence spectrometers. In order to select the optimal values of the influencing quantities when determining the chemical composition of copper alloys, a robust parameter design of a quantitative chemical analysis procedure was carried out using X-50 Mobile X-ray fluorescence spectrometer. The use of robust parameter design as opposed to conducting a full factorial experiment when developing a measurement procedure makes it possible to optimize the measurement conditions and obtain results of the required accuracy with a limited number of experiments and a maximum number of controlled factors. An example of drawing up an experimental plan for the parameter design of such procedure is provided, and a statistical analysis of the measurement results is carried out. The authors have analyzed and selected the optimal measurement conditions (influencing quantities), which ensure the minimum error of the results of measuring the mass fraction of elements. By selecting the optimal values of the influencing quantities based on the results of robust parameter design of the quantitative chemical analysis procedure, it became possible to increase the accuracy of determining the chemical composition of copper alloys and, hence, improve the reliability of the product quality control results at a relatively low cost. Such approach can be recommended for use by analytical laboratories developing procedures of quantitative chemical analysis for metallurgical enterprises.

Keywords Measurement procedure · X-ray fluorescence method · Spectrometer · Chemical composition · Copper alloys · Robust design of experiment · Measurement error

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Introduction

Associated with the use of copper and copper alloys is the development of such priority sectors of economic activity as construction, energy, machine-building, cable and wire manufacturing, automotive industry, and microprocessor and electronics production. In recent years, the consumption of copper industry products has been rapidly increasing. According to analytical data[1], in 2022, the consumption of copper products in Russia (wire rods, wire, and powders) increased by 27% (up to 393 mln kg) due to the expansion of the cable and wire manufacturing and construction industries. A large number of casting and wrought alloys are produced based on copper. The most common copper alloys are brass and bronzes. Brass is a binary or multicomponent alloy based on copper with the main alloying component being zinc (up to 50%). Bronzes are named depending on their main alloying elements. The most common are tin bronzes (up to 10% Sn), aluminum bronzes (9–10% Al), manganese bronzes (4–8% Mn), beryllium bronzes (0.5–3% Be), etc. Depending on the content of alloying elements (additives), such as phosphorus, zinc, lead, iron, manganese, nickel, etc., copper alloys are characterized by a wide range of electrical, mechanical, antifriction, technological, and corrosion resistance properties.

In order to obtain reliable information about the chemical composition of copper alloys, standardized measurement procedures (methods) are used. In particular, electrogravimetric and titrimetric methods are used to determine copper content in brasses and bronzes; titrimetric, polarographic, and atomic absorption methods—to determine zinc content; and titrimetric, photometric, and atomic absorption methods—to determine iron content. The mass fraction of tin in brasses and bronzes is established by using gravimetric, titrimetric, polarographic, photometric, and atomic absorption methods. However, the aforementioned standardized methods for determining chemical composition were developed over 30 years ago and have long become outdated.

The interstate standard (GOST 30608-98[2]) regulates the multi-element X-ray fluorescence method for quantitative chemical analysis of tin bronze samples for the contents of zinc, tin, iron, and other elements using a scanning or multichannel X-ray fluorescence spectrometer. However, in order to determine chemical composition, it is necessary to calibrate the spectrometer using reference standards (RS) of the tin bronze composition.

In recent decades, a number of highly effective instrumental analytical methods have been developed, offering an opportunity for their widespread application to perform rapid analytical monitoring of various substances and materials. Chemical methods (e.g., titrimetry, gravimetry, photometry) currently do not possess such important characteristics as rapidity, multi-element capability, and universality. Moreover, chemical methods are labor-intensive and not always amenable to automation.

The X-ray fluorescence analysis is promising method of analytical monitoring [1]. It does not utilize expensive and environmentally hazardous chemical reagents, while ensuring high capacity and rapidity of analysis. The advantages of the method also include multi-element capability, high precision and reproducibility of the results, a possibility of non-destructive monitoring, and a wide range of determining mass fractions of elements. The main drawback of such method has to do with the matrix effects. Due to practically non-existent composition reference standards, calibration curves are often constructed by using samples analyzed by different methods, or by using prepared model samples [2].

Currently, for solving a wide range of tasks at a minimum cost, portable compact X-ray fluorescence spectrometers are often used [3–5], such as an X-50 Mobile X-ray fluorescence spectrometer manufactured by Innov-X Systems, Inc. (USA). This spectrometer is designed for determining chemical elements in samples of metals, steels, and alloys, as well as for monitoring chemical composition of ores, soils, and other powdered and liquid samples [6]. The Research and Educational Center "Innovative Metallurgical Technologies" at the "MISiS" National University of Science and Technology uses such spectrometer to determine the chemical composition of copper alloys. The researchers at this Center have developed a procedure for determining the

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[1] "Vedomosti:" EU export of Russian-made copper dropped by five times. URL: https://www.vedomosti.ru/business/articles/2023/07/20/986108-eksport-rossiiskoi-medi-v-es-sokratilsya (access date: November 17, 2023).

[2] GOST 30608-98: Tin bronzes. Method of X-ray fluorescence analysis.

chemical composition of copper alloys by X-ray fluorescence using the X-50 Mobile spectrometer, while indicating the importance of selecting the optimal characteristics of the measurement conditions (influencing quantities).

The objective of this study is to perform a robust parameter design of the procedure for measuring the mass fraction of elements in copper alloy samples, and to establish the measurement conditions that ensure the minimum measurement error.

X-50 mobile X-ray fluorescence spectrometer. procedure for measuring the mass fractions of elements IN copper alloy SAMPLES

A set of analytical equipment (with a self-contained power supply) includes the X-50 Mobile X-ray fluorescence spectrometer, data collection and processing unit, power supply system (network adapter, batteries, and charger), and accessories for testing, transportation, and storage of the device. The spectrometer consists of an excitation source (X-ray tube, silver anode, 10–50 kV, 5–200 µA), detector (Si PiN diode, thermoelectric cooling using a Peltier element; spectral resolution of up to 230 eV along the Mn line (5.95 keV)).

An independent power supply, low weight (about 9 kg), and built-in safety systems make it possible to use this analytical equipment under the field and production conditions as a portable (mobile) system for analyzing the chemical composition of samples. The spectrometer's software provides the ability to process results based on the method of fundamental parameters, which enables the determination of the mass fraction of elements from the spectrum intensity without the use of reference standards [7]. Before performing measurements, the spectrometer is calibrated using the reference standard for steel AISI 316 (chemical composition: 66.345–74% Fe; 16–18% Cr; 10–14% Ni; 2.0–3.0% Mo; 2% Mn; 0.75% Si; 0.08% C; 0.045% P; 0.03% S; 0.10% N), the spectrum of which is stored in the device's reference spectrum library. The X-50 Mobile spectrometer is included in the State Register of Measuring Instruments (registration No. 43781-10). The relative error of measuring the mass fraction of elements is standardized within the following ranges: from 0.02% to ≤0.1%, from >0.1% to ≤5%, and from >5% to 99.9%, constituting 40, 15, and 10%, respectively.

Before measuring the mass fractions of elements, the operator selects the following measurement conditions: mode ("Analytical" or "Soils") and the number of repetitions. The "Analytical" mode is used for determining the chemical composition of metals and alloys, while the "Soils" mode—for determining the composition of soil samples and materials with a high content of light elements. In the "Analytical" mode, the operator can choose one of three additional functions, such as "Express sorting," "Precision," and "Disabled smart beam." The "Express sorting" function is designed for rapid determination of the alloy grade by comparing the obtained spectral characteristics of the sample with the spectral data for reference standards of different grades from the spectrometer database. The "Precision" function makes it possible to account for the effects of such elements as Cr, Ti, V, Mn, Fe, and Co, and enables detection of their presence (contents below 1%). During the analysis, two X-ray beams are used at X-ray tube voltages of 40 kV (beam 1) and 15 kV (beam 2). To obtain a general idea about the chemical composition of a sample, the exposure time can be 5 to 10 s. If a higher level of precision is required, or if the matrix composition of the analyzed samples may significantly affect the results, the exposure time is set at 10 to 20 s.

The "Disabled smart beam" function is intended for rapid qualitative and semi-quantitative determination of the chemical composition of alloys.

The accuracy of the results of measuring the mass fraction of elements also depends on the number of repetitions. The operator can specify the number of repetitions in the software ranging from 1 to 5.

To select the optimal values of the characteristics of influencing quantities when determining the chemical composition of copper alloys using the X-50 Mobile X-ray fluorescence spectrometer, a robust parameter design of the quantitative chemical analysis procedure was performed at the Research and Educational Center "Innovative Metallurgical Technologies."

Table 1 Noise factors at levels 1–5

N	RS1	RS2	RS3	RS4	RS5
$N1$ (Cu)	80.32±0.12	77.44±0.08	92.5±0.1	92.4±0.1	54.9±0.2
$N2$ (Zn)	0.57±0.05	1.06±0.04	2.78±0.04	4.03±0.05	37.3±0.3
$N3$ (Sn)	0.12±0.05	0.25±0.04	4.71±0.05	3.45±0.05	1.42±0.04
$N4$ (Fe)	4.37±0.05	5.05±0.05	0.023±0.007	0.116±0.035	0.56±0.02

Standardized method of robust parameter design

In laboratory practice, a variety of methodologies of full and fractional factorial design are commonly used [8, 9]. Fractional factorial design includes a robust parameter design of a system based on Taguchi methods. The system can be represented by a product, technology, procedure, etc. The standardized methodology is detailed in GOST R ISO 16336-2020[3].

The procedure for parameter design of a system includes the following main steps:

– determining the ideal system function—selection of the signal factor and output response;
– selecting noise factors and their levels;
– selecting controlled factors and their levels from the project parameters;
– distributing experimental factors between the internal and external tables;
– conducting the experiment and collecting data;
– calculating the signal-to-noise ratio and sensitivity, selecting the system with optimized parameters.

The algorithm and results of applying robust parameter design when developing procedures for testing geosynthetic materials and performing a quantitative chemical analysis in metallurgy are described in Ref. [10, 11].

Robust parameter design of the procedure for determining the chemical composition of copper alloys using the X-50 mobile spectrometer

The measurement procedure was considered as a system having a response in the form of an accuracy indicator (error) of the results of measuring the mass fraction of elements in copper alloys. When assessing robustness, the "smaller-the-better" procedure was used as recommended by GOST R ISO 16336-2020 for systems with a fixed value of the output variable. When calculating the error, the mass fractions of copper, zinc, tin, and iron (as specified in the RS certificates) were used as the reference values (Table 1). During the design of an experiment, the internal and external designs were formulated. For the internal design, controlled factors (F) were specified as the measurement conditions (influencing quantities) that can be unambiguously formulated by the developer (in the design of the quantitative chemical analysis procedure) and executed by the operator. The noise factors (N) included the variability of the test object characteristics, such as the chemical composition of the reference standard (mass fraction of elements in the sample, %). The studied objects included the reference standards of the composition of the following grades of bronze and brass: BrAZhNMts9-4-4-1 according to GOST 18175-

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[3] GOST R ISO 16336-2020: Statistical methods. Applications to new technologies and product development process. Robust parameter design (RPD).

[4] GOST 18175-78: Formable tin-free bronzes. Grades.

[5] GOST 5017-2006: Formable tin bronzes. Grades.

Table 2 Controlled factors at levels 1–2

F	1	2
$F1$, $F2$, c	5	20
$F3$	2	5

Table 3 Internal design of an experiment

n	$F1$	$F2$	$F3$
1	1	1	1
2	1	2	2
3	2	1	2
4	2	2	1

according to GOST 18175-78[4] (RS1, RS2), BrOTs4-3 according to GOST 5017-2006[5] (RS3, RS4), and LZhS58-1-1 according to GOST 15527-2004[6] (RS5).

The basic information about noise factors (N) and controlled factors (F) at different levels is provided in Tables 1 and 2. Each level is characterized by corresponding maximum and minimum values of the controlled factors. The noise factors include sample mass fractions of Cu, Zn, Sn, and Fe, % ($N1$ (Cu), $N2$ (Zn), $N3$ (Sn), $N4$ (Fe), respectively). The chemical composition of five reference standards are characterized by corresponding levels of noise factors (see Table 1). The controlled factors shown in Table 2 are represented by the exposure times of beams 1 and 2, s ($F1$ and $F2$ respectively) and the number of repetitions ($F3$).

The arrangement of controlled factors in the internal design of experiment during the development of the procedure is shown in Table 3, where n is the experiment number, and $F1$, $F2$, and $F3$ are the controlled factors listed in columns. The combinations of levels of such factors are shown in rows.

The external designs include experimental values of the system response (measurement result errors—Δ_{ij}) at different combinations of the noise factor levels, as well as the signal-to-noise ratios (ηi). Table 4 illustrates the external designs of experiments (E = 1–4) to determine the error of measuring the mass fraction of Cu, Zn, Sn, and Fe, respectively. The number of rows corresponds to the number of experiments established in the internal design of experiment (for the provided example, $n = 4$), and the number of columns corresponds to the number of combinations of the noise factor levels (for the provided example, $5^1 = 5$). The values of η_i are calculated based on experimental data separately for each row of the external table, representing a set of conditions for measuring the mass fraction of each element (Cu, Zn, Sn, Fe) in the copper alloy. The dashes shown in Table 4 indicate that the mass fraction of the element is below the lower detection limit of the spectrometer.

The value of the signal-to-noise ratio (in decibels) for the ith combination of controlled factors ($i = 1, 2, \ldots, n$), is calculated using the following expression:

$$\eta_i = -10 \lg \hat{\sigma}_i^2 = 10 \lg \hat{\sigma}_i^{-2} \,,$$

where $\hat{\sigma}_i^2$ is the standard deviation of the error of measuring the mass fraction of an element.

$$\hat{\sigma}_i^2 = n^{-1} \left(\Delta_{i1}^2 + \Delta_{i2}^2 + \ldots + \Delta_{in}^2 \right) \,.$$

The results of calculating the standard deviation and signal-to-noise ratios when developing the procedure are also shown in Table 4. As mentioned earlier, when performing parameter design, the optimal robustness of the system is achieved at the maximum signal-to-noise ratio. Therefore, from all the considered combinations

[6] GOST 15527-2004: Formable copper-zinc alloys (brasses). Grades.

Table 4 External designs of experiments 1–4

n	NE1	NE2	NE3	NE4	NE5	$\hat{\sigma}_i^2$	η_i, dB
E = 1							
1	–0.31	–0.46	–0.19	–0.47	0.34	0.136	8.66
2	–0.06	–0.33	–0.25	–0.21	–0.12	0.047	**13.3**
3	–0.30	–0.38	–0.38	–0.36	0.30	0.120	9.22
4	–0.64	–0.32	–0.40	–0.34	0.37	0.185	7.33
E = 2							
1	–0.05	0.12	0.05	0.13	0.77	0.126	9.00
2	–0.02	0.02	0.11	0.14	0.57	0.071	**11.5**
3	–0.02	0.03	0.15	0.18	0.56	0.074	11.3
4	–0.05	0.00	0.19	0.21	1.56	0.503	2.98
E = 3							
1	–	0.08	0.15	0.06	0.01	0.008	20.9
2	–	0.06	–0.03	0.04	–0.11	0.005	**23.4**
3	0.07	0.07	0.03	0.13	–0.02	0.006	22.5
4	0.05	0.09	0.07	0.15	0.10	0.010	20.2
E = 4							
1	0.15	0.18	–	0.064	0.05	0.015	18.13
2	0.09	–0.04	–	0.004	0.02	0.003	**25.97**
3	0.25	0.16	0.027	0.034	0.06	0.019	17.28
4	0.28	0.14	0.025	0.024	0.05	0.020	16.92

of the levels of controlled factors, the design of the quantitative chemical analysis procedure was selected, for which the following equality holds true: $\eta_{opt} = \max\{\eta_i\}$. This criterion is satisfied by the results of measuring the mass fraction of the analyzed elements (copper, zinc, tin, and iron), obtained in experiment $n = 2$ (highlighted in semi-bold). Hence, the following optimal values of the measurement condition characteristics can be recommended when determining the chemical composition of copper alloys using the X-50 Mobile X-ray fluorescence spectrometer: exposure times—5 s (beam 1) and 20 s (beam 2), number of repetitions—5.

In assessing the reproducibility of the signal-to-noise ratio, a verification experiment was conducted under the selected values of the measurement conditions. The following reproducibility estimates were obtained in the form of standard deviations: 0.34 dB (3.8%) for copper, 0.2 dB (2.3%) for zinc, 0.3 dB (3.4%) for tin, and 0.34 dB (3.8%) for iron. The reproducibility parameters of the analytical procedure are used when calculating the error of measuring the element mass fraction in the copper alloy:

$$\Delta = \sqrt{\left(\Delta_s / \sqrt{3}\right)^2 + \sigma_r^2} ,$$

where Δ_s is the systematic error of the analytical procedure (relative error of measurements using X-50 Mobile spectrometer with a uniform probability distribution law and a coverage factor of $\sqrt{3}$), and σ_r is the random error of the results of analysis (estimated reproducibility of the analytical result).

To enhance the efficiency of the design of experiment procedure and subsequent statistical analysis of the obtained results, the authors of this paper recommend using a specialized software packages, such as STATISTICA [12], MiniTab [13], PTC Mathcad Prime [14], etc. However, not all the packages offer the option of selecting the noise factors.

Conclusion

By using a robust parameter design methodology when developing quantitative chemical analysis procedures, it becomes possible to obtain the required accuracy of the measurement results by designing and organizing an experiment with a limited number of trials and the maximum number of controlled factors. Such design approach was used during the development of the procedure for determining the chemical composition of copper alloys to establish the values of the measurement condition characteristics (e.g., exposure times for beams 1 and 2, and number of repetitions) to ensure the minimum measurement error. The positive effect from using the robust parameter design methodology is achieved by enhancing the reliability of the results of determining the chemical composition of copper alloys and, hence, the results of assessing the product conformity to the specifications by implementing a relatively low-cost quality control procedures at the metallurgical plants.

Conflict of interest The authors declare no conflict of interest.

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